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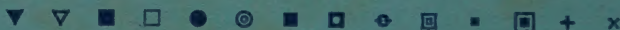
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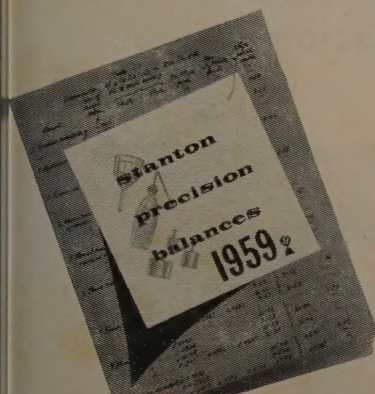
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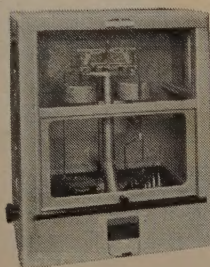
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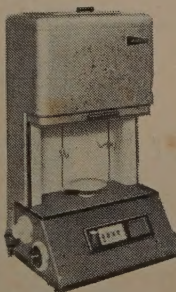
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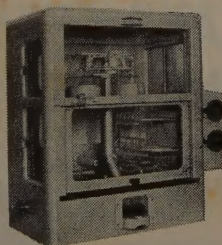


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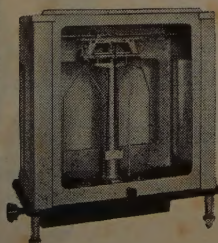
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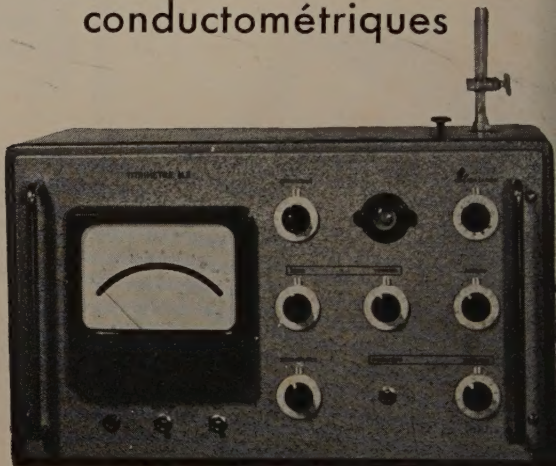
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THE SPECTROPHOTOMETRIC DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS. II

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INTRODUCTION

Some recent advances and improvements in this well established technique were described in a previous paper¹, which should be regarded as part I of this series. The techniques described therein have been used many times and have proved satisfactory. The object of the present paper is to provide data calculated from measurements of the unique range of spectra of the pure hydrocarbons employed in the previous investigation, which can be of use in routine analysis of complex mixtures of these hydrocarbons.

It is well known that in many combustion products, quantitative separation of the polycyclic aromatic hydrocarbons from each other is very difficult and in some cases impossible. Nevertheless, satisfactory determinations have been made by measuring the heights of absorption peaks characteristic of individual compounds in incompletely separated fractions.

EXPERIMENTAL

Full details of experimental procedure have been given in the previous paper for which a number of spectra were prepared which have been employed in the present investigation. Additional spectra were also prepared for the present work and one additional compound, 1 : 2, 3 : 4-dibenzpyrene, has been examined. The absorption peak heights were measured from tangents drawn to the minima on each side of the peak; the "base-line" technique^{2,3}. In the previous paper tables of absorbances (optical densities) were given for use with completely separated individuals but if the base-line technique is employed it is necessary to refer to calibration tables of heights measured in this way from standard spectra of pure compounds.

Table I is a list, arranged in chromatographic sequence, of the heights (in terms of O.D. or absorbance per μg per ml) so measured for a number of the more prominent absorption peaks. The spectra were determined in 1-cm silica cells as in the previous paper by means of a Beckman D.K.2 ratio-recording spectrophotometer.

In scanning spectra for identification of individual compounds a list of prominent peaks in wavelength order with the compounds corresponding to them is also of great value. Such a list is compiled in Table II.

During the compilation of these data an attempt was made to separate two isomeric dibenzpyrenes by repetitive alumina chromatography. A mixture of 1 : 2, 3 : 4- and 3 : 4, 9 : 10-dibenzpyrenes was not separated after passing through three successive columns, although the 3 : 4, 9 : 10-isomer appeared to be slightly more readily

TABLE I

CHROMATOGRAPHIC SEQUENCE OF ELUTION OF POLYCYCLIC AROMATIC HYDROCARBONS
FROM ACTIVE ALUMINA COLUMNS WITH CYCLOHEXANE

<i>Compound</i>	<i>Wavelength of peaks</i>	<i>Base-line factor (optical density for 1 μg/ml)</i>
Naphthalene	311	0.00156
Azulene	341	0.0194
	353	0.00807
2-Methylnaphthalene	305	0.00136
	320	0.00258
Acenaphthene	288	0.0127
	300	0.00815
	307	0.00734
	321	0.00942
Acenaphthylene	323	0.0255
	335	0.0097
	340	0.0184
Fluorene	221	no base to peak
	265	0.106
	301	0.0515
Phenanthrene	252	0.341
	293	0.0725
Anthracene	253	0.925
	340	0.0191
	357	0.0386
	376	0.0460
Pyrene	273	0.242
	320	0.117
	335	0.278
Fluoranthene	237	0.180
	288	0.222
3-Methylpyrene	243	0.268
	276	0.224
	344	0.181
1 : 2, 3 : 4-Dibenzanthracene	323	0.0014
	333	0.00516
	350	0.00812
1 : 2-Benzanthracene	278	0.188
	289	0.346
Chrysene	269	0.524
	294	0.0160
	306	0.0277
	320	0.0456
Naphthacene	441	0.0372
	471	0.0472
Perylene	253	0.0920
	409	0.0590
	437	0.119

TABLE I (continued)

<i>Compound</i>	<i>Wavelength of peaks</i>	<i>Base-line factor (optical density for 1 µg/ml)</i>
1 : 2-Benzpyrene	278	0.131
	290	0.168
	317	0.0500
	332	0.138
3 : 4-Benzpyrene	266	0.147
	285	0.164
	297	0.260
	364	0.0618
	385	0.101
	404	0.0164
1 : 12-Benzperylene	289	0.0640
	300	0.149
	363	0.0470
	384	0.0805
Anthanthrene	233	0.146
	307	0.242
	430	0.232
Coronene	302	0.668
	339	0.166
3 : 4, 9 : 10-Dibenzpyrene	242	0.234
	295	0.186
	372	0.148
	394	0.262
1 : 2, 3 : 4-Dibenzpyrene	290	0.0228
	331	0.0557
	401	0.0182

TABLE II

<i>Wavelength</i>	<i>Compound</i>	<i>Wavelength</i>	<i>Compound</i>
471	Naphthacene	350	1 : 2, 3 : 4-Dibenzanthracene
441	Naphthacene	344	3-Methylpyrene
437	Perylene	341	Azulene
430	Anthanthrene		
409	Perylene		
404	3 : 4-Benzpyrene	340	Acenaphthylene, Anthracene
401	1 : 2, 3 : 4-Dibenzpyrene	339	Coronene
394	3 : 4, 9 : 10-Dibenzpyrene	335	Acenaphthylene, Pyrene
385	3 : 4-Benzpyrene	333	1 : 2, 3 : 4-Dibenzanthracene
384	1 : 12-Benzperylene	332	1 : 2-Benzpyrene
380	Anthanthrene		
376	Anthracene	331	1 : 2, 3 : 4-Dibenzpyrene
372	3 : 4, 9 : 10-Dibenzpyrene	323	Acenaphthylene, 1 : 2, 3 : 4-Dibenz- anthracene
364	3 : 4-Benzpyrene	321	Acenaphthene
363	1 : 12-Benzperylene	320	2-Methylnaphthalene, Pyrene, Chrysene
357	Anthracene		
353	Azulene	317	1 : 2-Benzpyrene

TABLE II (continued)

Wavelength	Compound	Wavelength	Compound
311	Naphthalene	278	1 : 2-Benzanthracene, 1 : 2-Benzpyrene
307	Acenaphthene, Anthanthrene	276	3-Methylpyrene
306	Chrysene	273	Pyrene
305	2-Methylnaphthalene	270	Naphthacene
302	Coronene	269	Chrysene
301	Fluorene	266	3 : 4-Benzpyrene
300	Acenaphthene, 1 : 12-Benzperylene	265	Fluorene
297	3 : 4-Benzpyrene	261	Benzene
295	3 : 4, 9 : 10-Dibenzpyrene	255	Benzene
294	Chrysene	253	Anthracene, Perylene
293	Phenanthrene	252	Phenanthrene
290	1 : 2-Benzpyrene, 1 : 2, 3 : 4-Dibenzpyrene	249	Benzene
289	1 : 2-Benzanthracene, 1 : 12-Benzperylene	243	3-Methylpyrene
288	Acenaphthene, Fluoranthene	242	3 : 4, 9 : 10-Dibenzpyrene
285	3 : 4-Benzpyrene	237	Fluoranthene
		233	Anthanthrene
		221	Fluorene

eluted. It is therefore unlikely that these two compounds will be separable from mixtures containing them both, but they can be recognised when present together.

It should be noted that use of the factors given in the tables can provide in many cases only approximately quantitative amounts, and that the accuracy is improved with solutions containing fewer constituents. However, with repetitive determinations on a large number of samples, the approximate method is much faster and gives useful comparative results.

ACKNOWLEDGEMENT

The author thanks the Medical Research Council for supporting this investigation by the loan of equipment and provision of technical assistance.

SUMMARY

In repetitive determinations of polycyclic aromatic hydrocarbons in combustion products the use of incompletely separated chromatographic fractions is often an advantage favouring rapid work. Such fractions may be submitted to an approximate quantitative analysis by using tables of absorption peak heights measured from a base-line drawn between the minima on each side of the peak. Convenient tables for this method are provided in this paper.

RÉSUMÉ

Lors des dosages d'hydrocarbures aromatiques polycycliques dans des produits de combustion, il est souvent plus avantageux d'utiliser des fractions chromatographiques, incomplètement séparées. Des tables sont proposées pour effectuer cette détermination.

ZUSAMMENFASSUNG

Die Serien-Bestimmungen von polycyclischen aromatischen Kohlenwasserstoffen in Verbrennungsprodukten durch chromatographische Trennung können oft rascher durchgeführt werden, wenn hierzu nicht-vollständig getrennte chromatographische Fraktionen verwendet werden. Eine angenähert quantitative Auswertung der Ergebnisse kann mit Hilfe der gegebenen Tabellen erfolgen.

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR ANIONS. IV

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A systematic scheme^{1,2} of qualitative analysis for anions has been put forward from this laboratory. In the first paper it was pointed out that there are three problems (a), (b) and (c) that must be investigated carefully, if the sodium carbonate filtrate is to be used for the systematic separation of anions into groups in a satisfactory manner. This paper embodies the results of investigating problem (b) in a systematic manner. It has been found that the number of elements that pass into the 10% sodium carbonate filtrate is very much larger than is usually supposed, though the amounts of many elements present under ordinary circumstances are small. Luckily the presence of these elements in this filtrate does not interfere with the detection of the anions and the scheme that has been worked out remains practically unaltered as far as the detection of anions is concerned.

The present investigation has enabled us not only to get a clear picture of the distribution of the basic radicals in the different groups, but also to provide for their detection, if necessary, without interfering with the detection of the anions. If the sodium carbonate filtrate is to be tested for the anions only, the tests for the basic radicals can be omitted. If on the other hand the sodium carbonate filtrate is to be used for the detection of both basic radicals and anions, the tests for the basic radicals can be applied in addition to those for the anions. It can, however, be seen from Table I that under certain circumstances some basic radicals (Pt, Ru, Rh, Ga, Ge, Tl⁺, Re), which are tested for in the solution prepared with conc. HNO₃ and HCl, may pass completely into the sodium carbonate filtrate, and to ensure their detection it is necessary to test for them in this filtrate also.

A detailed knowledge of the distribution of both basic radicals and anions in the sodium carbonate filtrate is especially necessary, if a systematic and integrated scheme for the detection of basic radicals, anions and insoluble substances is to be worked out. The possibilities of devising such a comprehensive scheme are being explored in this laboratory and it is hoped that with the completion of this work it will be possible to evolve an integrated scheme according to the procedure given on page 109. A general idea of the elements that pass into the sodium carbonate filtrate and their distribution in the different groups will be obtained from Table I. This table is the same in general outline as Table I of Part I, but differs from it in having a larger number of basic radicals in some groups. All the basic radicals that may be present with the anions are shown in this table, but those that partially pass into the sodium carbonate filtrate are printed in bold-face type. To avoid repetition the anions of the groups have not been given. In order to provide for the detection of basic radicals as well as anions in the sodium carbonate filtrate, some modifications had to be intro-

TABLE I

Sodium carbonate filtrate containing all the anions and some basic radicals. Treat with sufficient excess of PbCO_3 and filter

<p>↓ Ppt. Anions of the group + Ce, Hg, Ir, Os, Ru and Rh. See Table II</p>	<p>↓ Filt. Rest of the anions + Al, Be, Cu, Co, Ni, U, Ti, Fe⁺², (Hg), Ce, (Ir), Au, Th, Zr, Pt, Ga, Ge, (Ru), (Os), (Rh), Ti^{+4}, Re and rare earths. Treat with excess of $\text{Zn}(\text{NO}_3)_2$ or $\text{Zn}(\text{CH}_3\text{COO})_2$ and filter</p>	<p>↓ Ppt. Anions of the group ZnCO_3 + Al, Be, Cu, Co, Ni, U, Ti, Fe⁺², (Hg), Ce, (Ir), Au, Th, Zr, Pt, Ga, Ge, (Ru), (Os) and (Rh) + (rare earths). Treat with excess of dil. NH_4OH and filter</p>	<p>↓ Filt. Rest of the anions + Au, traces of Be, Co, Ni, (rare earths) + (AsO_3^{-3}), Ti^{+4} and Re.</p>
<p>↓ Ppt. Anions of the group + Al, Be, Ce, (Ir), Ti, Fe⁺², Zr, Th, Ru and (Rh) + (rare earths). See Table III</p>	<p>↓ Filt. Rest of the anions + Al, Be, Cu, Co, Ni, U, (Hg), (Ir), Pt, Ga, Ge, (Os) and (Rh). Add magnesia mixture and conc. NH_4OH, heat and filter</p>	<p>↓ Filt. Rest of the anions + Cu, Co, Ni, U, (Hg), (Ir), (Os) and (Rh). Add Ca $(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ and filter</p>	<p>↓ Filt. Anions of the group + Cu, Co, Ni, U, (Hg), (Ir), (Os) and (Rh).</p>

Proceed as shown in Table I of ref.¹, first testing for Au in a portion of the filtrate with NaOH and Na_2O_2

See Table III of ref.²

Lead salts of the group anions + **Os**, **Ru**, **Rh**, **Ce**, **Hg**, **Ir** and **PbCO₃**. If the precipitate is black or grey in colour, test a portion for sulphide with **Zn** and conc. **HCl**. Dissolve the precipitate in dil. **HNO₃**, distil the solution with conc. **HNO₃** and collect the distillate in 6 *N* **NaOH** solution

Res. Nitrates of Ru , Rh , Ce , Hg , Ir and Pb . Add 2–3 g of KBrO₃ and distil again, collect the distillate in a hot solution of Ba(OH)₂	Dist. Heat to boiling and filter off barium ruthenate. Dissolve the precipitate in HCl and test for Ru with thio-urea	Dist. Yellow to red solution of sodium osmate. Acidify with HCl and test for Os with KCNS and ether or thio-urea
Res. Nitrates of Rh , Ce , Hg , Ir and Pb . Evaporate almost to dryness, take up the residue with dil. HCl and filter		
Ppt. PbCl₂ Reject.	Filt. Chlorides of Rh , Ce , Hg , Ir and (Pb). Add freshly prepared 2 <i>N</i> Na₂S reagent in excess followed by an equal vol. of conc. HCl and 2–3 g of ammonium acetate. Heat to boiling and filter	
	Ppt. Sulphides of Rh , Hg , Ir and (V). Treat with excess of Na₂S reagent and filter	
	Ppt. Rh₂S₃ , confirm as usual. <i>Note:</i> Precipitated Rh₂S₃ like Re₂S₇ does not dissolve in Na₂S reagent	Chlorides of V , Ce and (Pb). Boil to remove H₂S and test for V with H₂O₂ . Add NaOH solution in excess to the same solution and heat to boiling. A yellow precipitate confirms Ce
	Filt. Thiosalts of Hg , Ir and (V). Add 2–3 g of ammonium acetate and filter.	
	Ppt. Thiosalts of Ir and (V). HgS . Confirm as usual	

TABLE III

Ppt. Zinc salts of the group anions + Zr , Th , Al , Be , Ti , Fe⁺² , Ce , (Ru), (rare earths) and traces of Rh , Ir , Au⁰ . Treat with excess of NaOH solution and filter		Filt. Zn⁺ rest of the anions + Al , Be , (Ru) and traces of Rh and Ir . Acidify with dil. HCl and filter
Ppt. Au⁰ , hydroxides and phosphates of Zr , Th , Ti , Ce , Fe⁺² (rare earths). Treat with dil. HNO₃ and filter		Filt. Zn + rest of the anions + Al , Be , (Ru) and traces of Rh and Ir . (a) Test a portion for IO₄⁻ as usual (Table I of ref. ²). (b) Distil the remaining portion with conc. HNO₃ + KBrO₃ and test the distillate for Ru . Evaporate the remaining solution to dryness, take up the residue with HCl and test for remaining anions and basic radicals as usual (Table I of ref. ²) The traces of Rh and Ir present here need not be tested for
Ppt. Zr(HPO₄)₂ and Au⁰ . Test as usual for Zr and PO₄⁻³	Filt. Th , PO₄⁻³ , Zr , Fe⁺² , Ti , Ce and (rare earths). Test as usual for cations and PO₄⁻³ (Tables VI and VIII of ref. ⁴)	

TABLE IV

Ppt. Magnesium salts of AsO_4^{3-} , AsO_3^{3-} , PO_4^{3-} , PO_3^{3-} , TeO_3^{2-} , SiO_3^{2-} , SbO_4^{3-} , SbO_3^{3-} ^a and SnO_3^{2-} ^b + Al, Be, Pt, Ga and Ge . Treat with excess of dil. CH_3COOH and filter	
Ppt. TeO_3^{2-} , (AlPO ₄), phosphate and arsenite of Ga + Pt . Dissolve in dil. HCl . Add excess of freshly prepared 2 <i>N</i> Na_2S reagent followed by an equal vol. of conc. HCl . Heat to boiling and filter	Filt. Rest of the anions + Al, Be, (Pt) , Ga and Ge . Add $\text{Ca}(\text{NO}_3)_2$ solution in slight excess and filter
Ppt. sulphides of Pt . PO_4^{3-} , chlorides of Ga and (Al). Pt , Te and As . Test as usual (Table II of ref. ⁴)	Filt. Rest of the anions + Al, Be, (Pt) , Ga and Ge . (a) Add sodium phosphate to a portion and if any precipitate is obtained, test it for Ga . (b) Neutralize the excess of acid with NaOH and then add freshly prepared 1 <i>N</i> Na_2S in excess and filter
	Ppt. Anions of the group + Al, Be, Ca and Mg . Test as usual (Table II of ref. ²)
	Filt. Thiosalts of the anions + (Pt), Ge and Ga . Proceed as indicated previously (Table II of ref. ²), testing for Ge in the precipitate of As_2S_3 , TeS_2 by distillation with HCl + KClO_3 . Traces of Pt need not be tested for

^a In Table I of part I and Table II of part II SbO_3^{3-} has inadvertently been given as SbO_2^{2-} in some places.

^b All the tin is present here in the form of stannate. In previous papers^{1,2} the presence of stannite in this precipitate has mistakenly been indicated.

TABLE V

Filtrate from $\text{Ba}(\text{NO}_3)_2$, containing the rest of the anions + basic radicals shown previously (Table V of ref. ²), (AsO_3^{3-}), Ti^{+} , Re . Add AgNO_3 solution in slight excess boil for 2-3 min and filter	
Ppt. AgCl , AgBr , AgI , AgCNS , AgIO_3 . Ag_2S , Ag_3PO_4 (from PO_2^{3-}) (Ag_3AsO_3). Treat with dil. HNO_3 and filter	Filt. Rest of the anions + Be, (Cd, Ca, Ba) , Ti^{+} , Re . Boil with a slight excess of Na_2CO_3 . filter and reject the precipitate. Treat the filtrate as indicated previously (Table V of ref. ²), to test for ClO_3^- and BrO_3^- as AgCl and AgBr . In the filtrate neutralize the acid with NaOH and add excess of Na_2S reagent and filter
Ppt. AgCl , AgBr , AgI , AgCNS , AgIO_3 . Test as usual Table V of ref. ²)	Filt. ClO_4^- and thiosalt of Re . (a) To a portion of the filtrate add an equal vol. of conc. HCl and 2-3 g of ammonium sulphate. Heat to boiling. A black ppt. confirms Re . (b) Acidify another portion with dil. H_2SO_4 and test for ClO_4^- as indicated previously (Table V of ref. ²)

Mixture

Boil with 10% sodium carbonate solution and filter

↓	↓
Ppt.	Filt.
Most of the basic radicals and insoluble substances. Subject the ppt. to standard acid treatment and filter	Practically all the anions and some basic radicals.. Analyse according to the present scheme for anions
↓	↓
Ppt.	Filt.
Insoluble substances. Analyse according to the scheme ³ for insoluble substances.	Basic radicals. Analyse according to the comprehensive scheme ⁴ for the detection of basic radicals

duced into the detailed analysis of the groups. These modifications will be clear from the tables.

The solubility of the rare earths in the sodium carbonate filtrate was in general found to increase with increasing atomic weight of the element; the first few rare earths (with the exception of cerium) are practically insoluble in the sodium carbonate solution, whereas those at the end of the series are completely soluble. The rare earths that dissolve in 10% sodium carbonate solution are precipitated almost completely by zinc acetate and are found together with Zr, Th, etc., as shown in Table III. The small amounts of the rare earths that pass into the filtrate after precipitation with zinc acetate are precipitated with the sodium sulphide reagent used in the last step of the group analysis (Table V) along with the sulphides of Ag, Mn, Tl, etc.

ACKNOWLEDGEMENT

The authors express their gratitude to the Scientific Research Committee, U.P.-Government, for granting a research assistantship to one of them (M. LAL).

SUMMARY

A comprehensive investigation has been undertaken to ascertain how the basic radicals that pass into the sodium carbonate filtrate are distributed among the various groups for the detection of anions. Methods for the detection of these basic radicals in the presence of the anions have been worked out in detail. It was found that the scheme for the detection of anions put forward previously remains unaffected by the presence of these basic radicals. It has been shown that the scheme for the detection of anions can be integrated with the comprehensive schemes for the detection of basic radicals and insoluble substances.

RÉSUMÉ

Une étude a été effectuée pour déterminer la répartition des radicaux basiques (obtenus par traitement au carbonate de sodium), dans les divers groupes de l'analyse des anions. L'auteur décrit aussi les méthodes d'identification de ces radicaux, en présence des anions.

ZUSAMMENFASSUNG

Es wird die Verteilung basischer Radikale in den einzelnen Gruppen der Anionen nach der Behandlung mit Natriumcarbonat untersucht. Die Identifizierung dieser Radikale neben den Anionen wird beschrieben.

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SEPARATIONS INVOLVING SULPHIDES

X. SEPARATION OF ZINC FROM SOME ELEMENTS THAT FORM THIOSALTS

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The separation of zinc from other elements which form insoluble sulphides is attained with difficulty because of the solubility of zinc sulphide in dilute hydrochloric acid and its insolubility in acetic acid. It can be separated easily only from those elements whose sulphides are insoluble in fairly strong solutions of hydrochloric acid. In the present investigation, the separation of zinc from some elements which form thiosalts is discussed. The general method adopted was to treat the solution containing the two metals with sodium sulphide reagent and hydrochloric acid. The sulphide of the element was filtered off, weighed after washing and the zinc in the filtrate was estimated as zinc ammonium phosphate.

EXPERIMENTAL

Separation of arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from zinc.

Standard solutions of sodium arsenate, antimony potassium tartrate, potassium tellurite, selenious acid, ammonium molybdate, mercuric chloride, auric chloride, platinum chloride or potassium perrhenate and zinc chloride (by dissolving zinc oxide in the minimum quantity of dilute hydrochloric acid) were used. Measured volumes of the two solutions were mixed together and subsequently treated with 2N sodium sulphide reagent in excess. The mixture containing the thiosalt and zinc sulphide was acidified with a measured quantity of hydrochloric acid, and then heated to boiling and allowed to cool to room temperature. The precipitate was filtered through a weighed sintered glass crucible (porosity 4) and the precipitated metals were estimated as As_2S_5^1 , Sb_2S_3^2 , TeS_2^1 , SeS_2^1 , $\text{MoS}_3 \cdot 2 \text{H}_2\text{O}^3$, HgS^4 , Au_2S_3^2 , $\text{PtS}_2 \cdot 3 \text{H}_2\text{O}^5$ or Re_2S_7^4 respectively.

The following points are to be observed in precipitating the sulphides.

1. If a white precipitate appears on mixing the two solutions, it should be dissolved in the minimum quantity of caustic soda.
2. In the case of mercury, the mixture should be first treated with ammonium hydroxide till a white turbidity appears.
3. The solution containing the thiosalt of arsenic, platinum or rhenium should be acidified with a measured quantity of concentrated hydrochloric acid to produce an acidity of approximately 6 N in the resultant mixture. In the case of other elements, the thiosalt is acidified with 2 N hydrochloric acid to produce an acidity of approximately 1 N in the final mixture.

4. In the case of platinum, the mixture after acidification should be treated with 5–15 g of ammonium acetate; in the case of rhenium, 10–15 g of ammonium sulphate should be used.

After filtration and removal of the sulphide, the filtrate was evaporated to about 10 ml to remove hydrogen sulphide, diluted to 250 ml and zinc was estimated as $\text{ZnNH}_4\text{PO}_4^6$.

31–39 mg of arsenic, 48–62 mg of antimony, 55–69 mg of tellurium, 42–53 mg of selenium, 42–53 mg of molybdenum, 68–85 mg of mercury or 9–12 mg of gold were separated from 32–39 mg of zinc; 35–44 mg of platinum or 56–57 mg of rhenium were separated from 47–48 mg of zinc.

RESULTS

The metals were recovered with an accuracy of

As 0.0% to -0.3% and Zn + 0.46% to -0.23%
 Sb + 0.29% to -0.23% and Zn + 0.23% to -0.18%
 Te 0.0% to -0.38% and Zn + 0.46% to 0.0%
 Se \pm 0.2% and Zn + 0.37% to -0.46%
 Mo + 0.15% to 0.0% and Zn + 0.18% to -0.46%
 Hg + 0.4% to 0.0% and Zn + 0.18% to -0.23%
 Au 0.0% and Zn + 0.37% to -0.46%
 Pt 0.0% to -0.2% and Zn 0.0% to -0.46%
 Re + 0.22% to 0.0% and Zn + 0.46% to 0.0%

SUMMARY

It has been shown that 2 N sodium sulphide reagent can be used for separating arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from zinc.

RÉSUMÉ

On a pu séparer quantitativement le zinc d'avec l'arsenic, l'antimoine, le tellure, le sélénium, le molybdène, le mercure, l'or, le platine ou le rhénium au moyen d'une solution 2 N de sulfure de sodium.

ZUSAMMENFASSUNG

Zink lässt sich mit Hilfe einer 2 N Natriumsulfidlösung von Arsen, Antimon, Tellur, Selen, Molybdän, Quecksilber, Gold, Platin oder Rhenium quantitativ trennen.

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THERMOMETRIC TITRATION OF URANIUM(IV) WITH POTASSIUM DICHROMATE

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INTRODUCTION

Thermometric methods of analysis have been known to analytical chemists since the pioneer work of DUTOIT AND GROBET¹. More recently MÜLLER² suggested the use of a thermistor as a heat-sensitive device to replace the Beckman thermometer that is still being used by some workers. LINDE *et al.*³ adapted a thermistor for use in automatic thermometric titrations. JORDAN AND ALLEMAN⁴ followed up the work of LINDE *et al.* by determining heats of chelation by thermometric titrations. JORDAN AND ALLEMAN⁴ have preferred to call the technique "enthalpymetric" titration as being a term which has greater relation to the fundamental, thermodynamic quantities upon which the technique is based. Their argument is based upon the equation.

$$\Delta H = \Delta F - T\Delta S$$

ΔH = enthalpy change, cal/mole

ΔF = free energy change, cal/mole

T = temperature, °K and

ΔS = entropy change, cal/mole.

The equation indicates that a thermometric titration is sensitive not only to a reaction in which there is a change in free energy but also to one in which the entropy change is significantly large although the free-energy change is small. Accordingly, consideration given to available thermodynamic data may often determine the feasibility of a thermometric titration without experimental work.

The application of the thermometric method to redox titrations was suggested in the article by LINDE *et al.*³ One of the titrations which appeared feasible was the thermometric titration of uranium(IV) with potassium dichromate.

KOLTHOFF AND LINGANE⁵ appear to be the first to have recommended the use of potassium dichromate as a reagent for the quantitative oxidation of uranium(IV) to uranium(VI). Diphenylamine sulfonate may be used as the indicator. Either diphenylamine or diphenylbenzidine, each with the addition of some ferric iron to the solution, is also satisfactory. The dichromate titration of uranium(IV) is now well known. The potentiometric method of titration in which a noble-metal, indicator electrode and any one of various reference electrodes are used is a commonly accepted method of titration.

The electrode mechanism involving dichromate with a bright platinum electrode is not well understood. There is a variance in observed potential with a change in pH

* Operated by Union Carbide Corporation for the Atomic Energy Commission.

of the solution⁶. In addition, from the authors' experience, the platinum electrode, when used as an indicator electrode in redox titrations in the presence of chromium ion, required frequent cleaning and treatment. In some cases after protracted use in solutions containing chromium ions, cleaning of the electrode failed to restore it and replacement was necessary.

EXPERIMENTAL

The experimental arrangement was essentially that suggested by LINDE, ROGERS AND HUME³ and used later by JORDAN AND ALLEMAN⁴. The required equipment was as follows:

Microburet; constant-speed, syringe-type, 1-ml capacity, made by the Greiner Co. The microburet was driven by a constant-speed motor, available from the Bodine Co., through a gear arrangement.

Stirring motor; 1600-r.p.m., constant-speed, available from the A. S. LaPine Co. Only the slow-speed shaft that operates at a 5.3-reduction of the 1600-r.p.m. shaft was used. The stirring blade was a spiral made of a flattened piece of pyrex glass attached to a pyrex glass rod. The spiral design provides stirring in a vertical as well as a horizontal plane.

Dewar Flask; 250-ml, to provide adiabatic conditions for the titration. A cork stopper bored as to centre a 20-ml beaker was inserted in the bottom of the flask. The flask closure was a 3-hole cork stopper that provided access for the buret tip, the stirrer shaft, and the glass tube that supported the thermistor.

Thermistor and Recorder. A thermistor was used as a temperature-sensing device. Since a thermistor is essentially a nonlinear resistance element that changes resistance with temperature, it was coupled as an element of a Wheatstone bridge, to which a potential of 1.5 V was supplied by a dry-cell battery. The unbalance potential of the bridge was fed to a Brown recording potentiometer that was set to read 5 mV at full scale. Because the chart paper of the recorder is driven at a constant rate, a direct calibration was made between the inches of chart travel and volume of titrant added by the constant-speed microburet.

The procedure for carrying out the titration was as follows: Five ml of 1.0 *N* H₂SO₄ solution was pipeted into a 10-ml polyethylene beaker. Test solution was added, but the total volume was not allowed to exceed 6 ml. The beaker was placed in the Dewar flask. The Dewar flask was placed in position on the ring stand and was clamped there. The stirring motor was started and a short interval of time was allowed for thermal equilibration. The Brown recorder was started

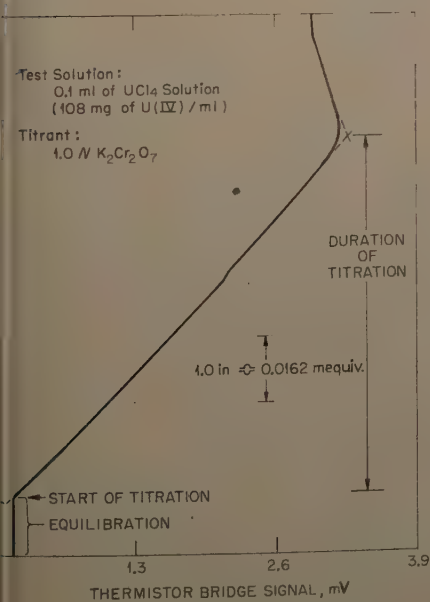


Fig. 1. Typical titration curve.

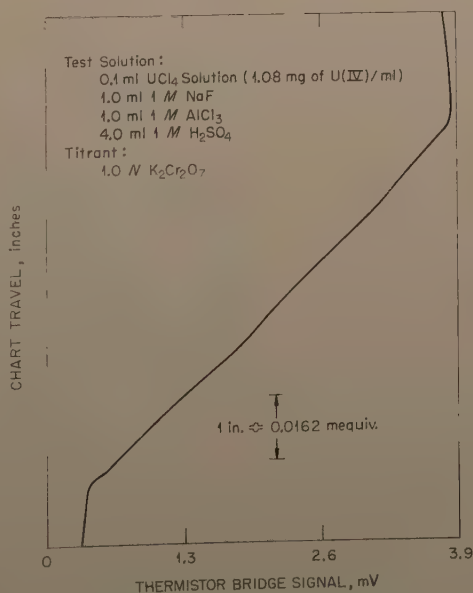


Fig. 2. Titration curve for simulated sample solution.

and standardized. The thermistor bridge was turned on. The buret drive was started, and the recorder chart was marked simultaneously to show the starting point of the titration. After the termination of the titration, the first two legs of the curve that was plotted on the recorder chart were extrapolated to their point of intersection. The distance from the starting point to the point of intersection was a measure of the volume of titrant required to complete the titration (Fig. 1).

The titrant that was used in the series of titrations under discussion was 1.0 *N* potassium dichromate and was prepared by weighing out primary standard potassium dichromate. The diluent was 1.0 *N* H₂SO₄ solution prepared by the dilution of analytical reagent-grade concentrated sulfuric acid.

DISCUSSION

It has been stated³ that a redox titration can be followed by the measurement of the heat change involved in the reaction. Accordingly, an investigation, described herein, of the thermometric titration of uranium(IV) with potassium dichromate in solutions that contain uranium(IV), zirconium(IV), aluminium(III), fluoride, chloride, and sulfate ions has shown that the titration is feasible (Fig. 2).

The results of a series of titrations are presented in Tables I and II that follow.

TABLE I

RESULTS OF THE TITRATION OF URANIUM TETRACHLORIDE

Titrant: 1.0 *N* K₂Cr₂O₇. Sample solution: UCl₄ in HCl solution; 108 mg of U(IV)/ml. Diluent: 1.0 *N* H₂SO₄ solution. Volume of test portion: 0.10 ml. Chart calibration: 1 inch of chart travel \approx 0.0162 mequiv.

Test No.	Chart travel inches
1	5.60
2	5.60
3	5.62
4	5.60
5	5.62
Average	5.61

Relative standard error at 95% probability level = $\pm 0.25\%$

TABLE II

RESULTS OF TITRATION OF SOLUTIONS OF URANIUM TETRACHLORIDE THAT CONTAINED SODIUM FLUORIDE AND ALUMINIUM CHLORIDE

Titrant: 1.0 *N* K₂Cr₂O₇. Sample solution: UCl₄ in HCl solution, 108 mg of U(IV)/ml. Diluent: 1.0 *N* H₂SO₄. Volume of test portion: 0.10 ml. Chart calibration: 1 inch of chart travel \approx 0.0162 mequiv. Added to each test portion: 1.0 ml of 1.0 *M* NaF and 1.0 ml of 1.0 *M* AlCl₃

Test No.	Chart travel inches
1	5.63
2	5.65
3	5.60
4	5.70
5	5.60
Average	5.64

Relative standard error at 95% probability level = $\pm 1.03\%$

The test solution was a solution of uranium tetrachloride originally estimated to contain 116 mg of uranium(IV) per ml. The uranium(IV) content gradually decreased because of air oxidation. At the time the test solution was analysed, the uranium(IV) content was estimated to be 108 mg/ml. No attempt was made to stabilize the solution. The precision data were obtained by making a series of titrations as quickly as possible in order to minimize the change in the uranium(IV) content.

Table III gives the results of a test run on an actual sample; the run was made for the purpose of establishing the bias. The sample was a solid derived from a fused-salt melt of zirconium fluoride and uranium fluoride. A 1.2958-g portion of this sample was dissolved by the use of aluminum chloride and sulfuric acid according to the procedure developed by ANONSEN AND FRENCH⁷. The resulting solution was diluted to a final volume of 50 ml with water. Aliquots were withdrawn from this final volume for titration. A plot of the data of Table III indicates the lack of bias in the method (Fig. 3).

TABLE III

RESULTS OF TITRATION OF URANIUM(IV) IN SAMPLE SOLUTION OF ZIRCONIUM FLUORIDE AND URANIUM FLUORIDE

Titrant: 1.0 N $\text{K}_2\text{Cr}_2\text{O}_7$. Diluent: 1.0 N H_2SO_4 . Sample: $\text{ZrF}_4\text{-UF}_4$ dissolved in $\text{AlCl}_3\text{-H}_2\text{SO}_4$ solution¹. Uranium (IV) content: 1.54 mg/ml. Chart calibration: 1 inch of chart travel \approx 0.0162 mequiv.

Test No.	Volume of test portion, ml	Chart travel inches
1	1.00	0.80
2	2.00	1.65
3	3.00	2.45
4	4.00	3.20
5	5.00	4.35

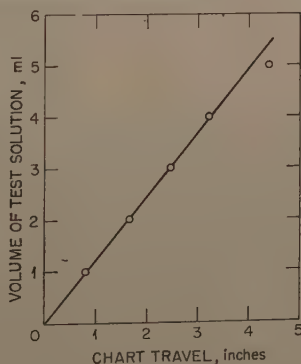


Fig. 3. Bias test (Data of Table III)

The applicability of the thermometric technique to the redox titration of a solution of uranium(IV) with a standard solution of potassium dichromate has been demonstrated. The thermometric technique offers an advantage over the potentiometric method in that the difficulties associated with the use of a noble-metal, indicator electrode are avoided⁶.

ACKNOWLEDGEMENT

Dr. M. T. KELLEY gave us invaluable advice, and Mr. HAROLD C. JONES adapted the Greiner microburet to a constant-speed motor drive. We gratefully acknowledge their assistance.

SUMMARY

A thermometric method is presented for the redox titration of uranium(IV) with dichromate. The investigation was made primarily to determine the applicability of the thermometric method to redox titrations in solutions that contain ions deleterious to electrodes used in electrometric methods. A relative standard error of $\pm 1\%$ is attainable in the titration of quantities of uranium(IV) of the order of 5 mg. Less than 15 min is required to complete a titration. Fluoride ion can be tolerated in the solution provided that sufficient aluminum(III) is added to complex all the fluoride.

RÉSUMÉ

Une méthode thermométrique est proposée pour le titrage redox de l'uranium(IV) au moyen de dichromate. En présence d'ion fluorure, il est nécessaire d'ajouter de l'aluminium(III) en quantité suffisante pour le complexer totalement.

ZUSAMMENFASSUNG

Es wird eine thermometrische Methode zur Redox-Titration von Uran(IV) mit Dichromat beschrieben. Fluor-Ionen stören nicht, wenn sie durch Zugabe einer genügend grossen Menge von Aluminium(III) in die Komplexverbindung übergeführt werden.

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THERMAL DECOMPOSITION OF SOME RARE EARTH METAL CUPFERRATES AND NEOCUPFERRATES

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Cupferron (ammonium salt of *N*-nitrosophenylhydroxylamine) and neocupferron (ammonium salt of *N*-nitrosonaphthylhydroxylamine) have been proposed as organic precipitants for the gravimetric determination of the lighter rare earth elements¹. Previous thermobalance studies have shown that reagent is coprecipitated with the metal cupferrates, making it necessary to ignite and weigh as the metal oxides². The metal neocupferrates required the same procedure³.

As was anticipated, the heavier rare earth ions, those from europium to ytterbium, are also precipitated by these reagents. With the objective in mind that these two

agents may prove useful as analytical precipitants for the heavier rare earth metal ions, the metal cupferrates and neocupferrates were prepared and subjected to thermal decomposition on the thermobalance. Such information, as with the lighter rare earth metal chelates, is needed in order to determine the weighing form of the precipitates.

EXPERIMENTAL

Reagents

Cupferron and neocupferron were obtained from the Matheson, Coleman, and Bell Co., East Rutherford, N. J. They were used without further purification.

The rare earth samples were obtained as the oxides of 99.9% purity from Research Lab., Inc., Newtown, Ohio. The purity was that listed by the supplier.

All other reagents were of analytical reagent-grade quality.

Thermobalance

An automatic recording thermobalance which has previously been described was used⁴. The sample sizes ranged in weight from 60 to 90 mg and were run in duplicate or triplicate. A linear heating rate of 5.4° was used on all of the samples. During the pyrolysis of the samples, a slow stream of air was passed through the furnace to remove the decomposition products.

Preparation of chelates

The rare earth metal cupferrates and neocupferrates were prepared by the same general procedure as previously described¹. The precipitates were air dried at room temperature for 24 h before being pyrolyzed on the thermobalance.

DISCUSSION

The thermograms of the rare earth metal cupferrates and neocupferrates are given in Figs. 1 and 2 with the composition data given in Table I.

Europlum cupferrate

(Fig. 1F) The compound began to lose weight slowly beginning at 85°. At 150° the first break, but not a horizontal weight level, was found in the curve, followed by a very rapid weight loss above 170°. A second break in the curve was observed at 295° followed by further weight loss above 320°. An almost horizontal weight level was then found beginning at 415°, resulting in the formation of the oxide level, Eu_2O_3 , at 570°.

TABLE I

COMPOSITION DATA FOR RARE EARTH CUPFERRATES AND NEOCUPFERRATES

Rare earth	% Metal oxide			
	Cupferrate		Neocupferrate	
	Theoretical	Found	Theoretical	Found
Europlum	31.24	31.4 31.9	24.66	24.0 24.0
Terbium	32.78	32.8 32.6	25.94	25.2 25.3
Dysprosium	32.49	32.3 32.6	25.75	26.4 26.6
Holmium	32.78	29.6 29.6	26.00	24.9 24.9
Erbium	33.04	28.8 28.4	26.24	25.8 25.8
Thulium	32.71	33.4 33.1	26.82	24.8 24.8

Terbium cupferrate

(Fig. 1E) From the composition data, the air-dried chelate corresponded exactly to that expected for TbCup_3 ; where Cup is the cupferron ion. The first weight loss began at 85° , slowly at first, but becoming very rapid above 205° . A break in the curve was observed at 265° with further weight loss above 325° , resulting in the Tb_4O_7 level at 540° .

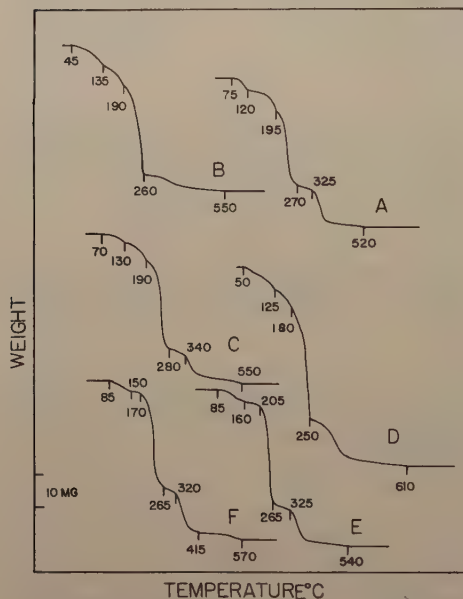


Fig. 1. Thermograms of the metal cupferrates. A. ytterbium, B. erbium, C. dysprosium, D. holmium, E. terbium, F. europium.

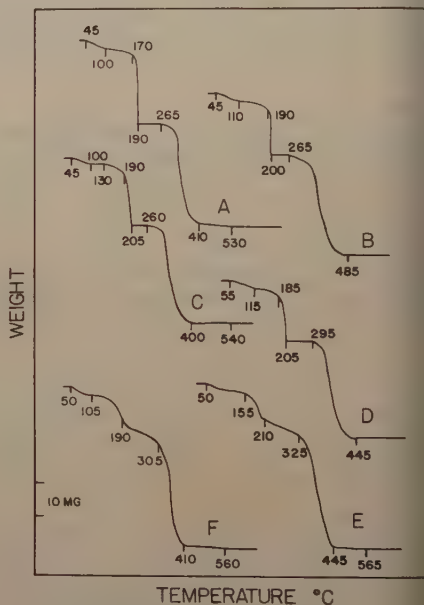


Fig. 2. Thermograms of the metal neocupferrates. A. erbium, B. ytterbium, C. dysprosium, D. holmium, E. terbium, F. europium.

Dysprosium cupferrate

(Fig. 1C) The composition of the chelate corresponded to the formula, DyCup_3 , when air dried at room temperature. The first weight loss began at 70° , somewhat less than that found for TbCup_3 . Breaks were observed in the curve at 130° , 190° , and 280° . The final oxidation of the organic matter began at about 340° , resulting in the Dy_2O_3 level at 550° .

Holmium cupferrate.

(Fig. 1D) This chelate began to lose weight at a low temperature, probably because of coprecipitated cupferron. The composition data shows a smaller percentage of oxide than the theoretical amount, indicating coprecipitation of reagent.

After the first weight loss at 50° , breaks in the curve were observed at 125° , 180° , and 250° . The final oxidation of the organic matter began at 250° , resulting in the Ho_2O_3 level at 610° .

erbium cupferrate

(Fig. 1B) This chelate was the least stable of all of the metal cupferrates studied. Again, as in the case of HoCuP_3 , this was probably due to coprecipitated reagent. The first weight loss began at 45° , with breaks in the curve at 135° , 160° , and 260° . The Er_2O_3 level began at 550° .

ytterbium cupferrate

(Fig. 1A) The first weight loss was observed at 75° , with breaks in the curve at 100° , 195° , and 270° . Final oxidation of the organic matter began at 325° , resulting in the Yb_2O_3 level at 520° .

europium neocupferrate

(Fig. 2F) The composition of the air-dried metal chelate corresponded approximately to the formula, $\text{Eu}(\text{Neocup})_3$; where Neocup is the neocupferron ion. The first weight loss was observed at 50° , with breaks in the curve at 105° and 190° . The initial weight loss did not correspond to the evolution of an entity of molecular weight 18 as was found in the lighter rare earth neocupferrates³. A horizontal weight level was not observed in the curve after this initial weight loss as was previously found. Beyond 305° the weight loss was quite rapid, resulting in the Eu_2O_3 level at 560° .

terbium neocupferrate

(Fig. 2E) The composition of the air-dried chelate corresponded closely to the formula, $\text{Tb}(\text{Neocup})_3$. The first weight loss began at 50° , slowly at first, but becoming quite rapid above 155° . A break in the curve was observed at 210° , with further rapid weight loss above 325° . The Tb_4O_7 level began at 565° .

dysprosium neocupferrate

(Fig. 2C) The first weight loss began at 45° with a horizontal weight level being observed from 100° to 130° . The composition of the curve in this region is not known. Beyond 190° the chelate decomposed very rapidly, forming another horizontal weight level from 205° to 260° . This same general thermogram pattern is different from the previous two chelates but similar to the neocupferrates of Ho, Yb, and Er. Above 260° the chelate decomposed rapidly, resulting in the Dy_2O_3 level at 540° .

holmium cupferrate

(Fig. 2D) The first weight loss began at 55° with a break in the curve, but not a horizontal weight level, at 115° . Beyond 185° the chelate decomposed rapidly, resulting in a horizontal weight level extending from 205 to 295° . The composition of the curve in this level is not known. Beyond 295° the organic matter began to oxidize rapidly, resulting in the Ho_2O_3 level at 445° .

ytterbium neocupferrate

(Fig. 2A) The air-dried chelate began to lose weight at 45° . After a break in the curve at 100° , the weight loss was quite slow until 170° . Above this temperature, the chelate lost weight rapidly, giving a horizontal weight level from 190 to 265° .

Beyond 265° the remaining organic matter oxidized rapidly, resulting in the Er_2O_3 level at 530° .

Ytterbium neocupferrate

(Fig. 2B) The first weight loss began at 45° , giving a break in the curve at 110° . Above this temperature the weight loss was slow until about 190° , where the weight loss became quite rapid. A horizontal weight level was then observed from 200 to 265° with additional rapid weight loss about 265° . The Yb_2O_3 level began at 485° .

General

In general, the heavier rare earth metal cupferrates and neocupferrates were less stable thermally than the corresponding lighter rare earth compounds. However, the minimum oxide level temperatures were in the same general temperature range.

The thermograms show that it is not possible to dry the precipitated complexes to constant weight and then weigh as the stoichiometric metal chelates. In several cases, the amount of metal oxide found for the metal chelates was less than the theoretical amount, indicating coprecipitation of the reagent. This phenomena was found even if a stoichiometrical amount of reagent was used to precipitate the rare earth metal ions.

The exact decomposition mechanism of the metal complexes is not known so it is difficult to assign definite compositions to all parts of the thermal decomposition curve. However, from the first weight loss temperature to the minimum oxide level temperature, the curve probably represents the resultant of a mixture of two or more different compounds. It appears fairly certain that the metal complexes are not hydrated so that the first weight losses are not due to the loss of hydrate-bound water.

SUMMARY

The thermal decomposition of the cupferrates and neocupferrates of europium, terbium, dysprosium, holmium, erbium, and ytterbium was studied on the thermobalance. The metal chelates possessed poor thermal stability as well as a pronounced tendency to coprecipitate reagent. The minimum oxide level temperatures for the metal cupferrates were: Eu, 570° ; Tb, 540° ; Dy, 550° ; Ho, 610° ; Er, 550° ; and Yb, 520° . The minimum oxide level temperatures for the metal neocupferrates were: Eu, 560° ; Tb, 565° ; Dy, 540° ; Ho, 445° ; Er, 530° ; and Yb, 485° .

RÉSUMÉ

On a examiné la décomposition thermique des cupferrates et néocupferrates d'euporium, de terbium, de dysprosium, d'holmium, d'erbium et d'ytterbium sur la thermobalance. Ces composés présentent une faible stabilité thermique.

ZUSAMMENFASSUNG

Es wurde die thermische Zersetzung der Kupferron- und Neokupferron-Komplexe von Europium, Terbium, Dysprosium, Holmium, Erbium und Ytterbium auf der Thermowage untersucht. Diese Verbindungen besitzen nur eine geringe Wärmestabilität.

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DETERMINATION OF NIOBIUM AND TANTALUM IN BINARY ALLOYS AND ZIRCONIUM ALLOYS

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INTRODUCTION

Preparation of zirconium alloys containing substantial amounts of niobium and tantalum, which have been proposed for use in nuclear reactors, and the development of niobium-tantalum alloys for evaluation of their properties, especially at elevated temperatures, created a need for rapid methods of determining niobium and tantalum in the presence of each other and in zirconium.

Provision of such methods is made more difficult because of the chemical similarity of these elements and the marked influence which they exercise on the normal reactions of each other in solution.

Published methods are intended principally for the examination of ores and minerals, and usually involve separation of niobium and tantalum from each other and from associated elements. Separation of niobium and tantalum from other elements has been achieved by chemical methods, *e.g.* selective precipitation of their fluorides, oxides or tannin complexes¹, and by physical methods, *e.g.* fractional distillation of their volatile chlorides². These procedures, however, are time-consuming and separations are often incomplete, especially in the presence of large amounts of zirconium (or titanium). More recently, chromatographic methods have been described^{3,4}, in which niobium and tantalum are extracted from a fluoride solution on a cellulose column, with ethyl methyl ketone containing dilute hydrofluoric acid. In this way, niobium and tantalum can be separated from the majority of metals. Other methods for separating niobium, tantalum, zirconium and titanium from one another are based on selective extraction from acid solution, by means of organic solvents such as isobutyl methyl ketone, di-isobutyl ketone or cyclohexanone⁵⁻⁷. After separation by any of these methods, niobium and tantalum are usually separately determined either by gravimetric or absorptiometric procedures.

Absorptiometric methods have been described for determining niobium and tantalum in ores¹ without recourse to a preliminary separation, unless significant amounts of interfering elements are present. Niobium has been determined by procedures based on the yellow colour formed when a solution of the metal reacts with thiocyanate ions in hydrochloric-tartaric acid solution containing acetone as a colour stabiliser^{8,9}, but in our experiments zirconium caused serious interference. A procedure depending on the formation of a yellow niobium-peroxide complex in sulphuric-phosphoric acid solution¹⁰, has also been described, but the reaction is not very sensitive. A colorimetric procedure, based on the formation of a tantalum-

catechol complex in hydrochloric-sulphuric-oxalic acid solution, has been described¹¹ for the determination of tantalum.

Both niobium and tantalum form soluble, yellow complexes with pyrogallol in ammonium oxalate solution^{12,13}. Tantalum is determined in acid pyrogallol solution and under these conditions, interference by niobium is small, but in alkaline pyrogallol solution the order of sensitivity is reversed.

All these colorimetric procedures are subject to interference by other metals, such as iron, molybdenum, tungsten and particularly titanium; where the effect is small a correction can often be applied, but significant amounts of these metals must be separated.

In order to provide methods for determining niobium and tantalum in their binary alloys and in zirconium, the pyrogallol reaction, because of its direct application to both niobium and tantalum, was selected for investigation.

EXPERIMENTAL

I. DETERMINATION OF NIOBIUM IN TANTALUM AND ZIRCONIUM

Preliminary experiments

Initial experiments were made (a) to determine the most suitable wavelength at which to measure absorption of the niobium-pyrogallol complex in the presence of tantalum and zirconium complexes; and (b) using this wavelength, to prepare a calibration graph. The concentrations of reagents used in this preliminary work were accurately controlled as recommended by HUNT AND WELLS¹³.

(a) *Absorption curves.* High purity niobium pentoxide (71.5 mg) was fused with 10 g of potassium bisulphate in a small platinum dish, and the cooled melt was extracted with about 200 ml of hot water containing 20 g of ammonium oxalate. The solution was diluted to 500 ml in a calibrated flask; then:

$$1 \text{ ml} \equiv 0.1 \text{ mg of niobium.}$$

To 2.5 ml of this solution, contained in a 50-ml calibrated flask, 17.5 ml of ammonium oxalate solution (4%) were added, followed by 4.5 ml of potassium bisulphate solution (10%), thus bringing the total amounts of these reagents in solution to 0.8 g and 0.5 g respectively. 20 ml of pyrogallol reagent (2.0% in 20% sodium sulphite solution) were added, the solution was diluted to the mark, then set aside for 15 min at 20°. O. D. measurements were made at wavelengths between 3600 Å and 4800 Å, using a Unicam S.P. 600 spectrophotometer and 2-cm cells.

Further absorption curves were prepared as described above, using:

- (1) reagents only, in order to ascertain blank values at various wavelengths;
- (2) 2.5 ml of tantalum solution
(1 ml \equiv 0.3 mg of tantalum);
- (3) 7.5 ml of zirconium solution
(1 ml \equiv 1.0 mg of zirconium).

None of the curves (Fig. 1) showed a peak of maximum absorption, and in every instance absorption decreased with increase in wavelength; the absorption/mg of metal was greatest for niobium and least for zirconium. The absorption-ratio curve of the niobium and tantalum complexes at various wavelengths (Fig. 2) approached

maximum at about 4500 Å, and this was also true for the absorption-ratio curve of the niobium and zirconium complexes. A wavelength of 4500 Å was therefore selected for preparation of calibration and correction graphs. At 4500 Å, absorption by the niobium complex was only about half that at 4100 Å, the wavelength recommended by HUNT AND WELLS¹³, but absorption by the tantalum or zirconium complexes at 4500 Å was about one fifth of that obtained at the lower wavelength.

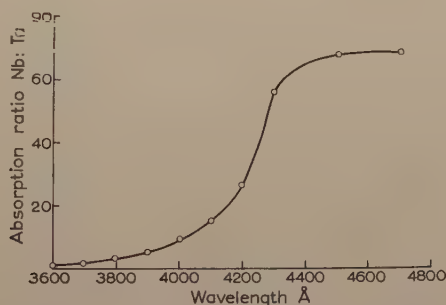
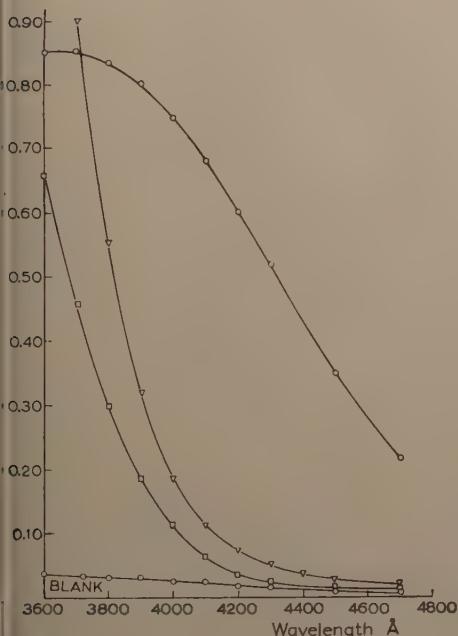


Fig. 2. Absorption ratio curve of niobium to tantalum pyrogallol complexes at various wavelengths. Niobium 0.25 mg/50 ml; tantalum 0.75 mg/50 ml; cell 2 cm.

Fig. 1. Absorption curves of niobium, tantalum and zirconium/pyrogallol complexes and "blank" solution (alkaline medium). Niobium \circ 0.25 mg/50 ml; tantalum \square 0.75 mg/50 ml; zirconium ∇ 7.5 mg/50 ml; cell 2 cm.

(b) *Calibration and correction graphs.* Volumes of niobium solution (1 ml \equiv 0.1 mg niobium) up to 5.0 ml were transferred to 50-ml calibrated flasks and reagents were added in accordance with the procedure outlined in (a), the weight of ammonium oxalate and potassium bisulphate being adjusted, as before, to 0.8 g and 0.5 g respectively. These solutions were diluted to the mark and optical densities were determined at 4500 Å, using 2-cm cells; a linear calibration graph was obtained. A differential calibration graph was also prepared, using solutions containing 1.0 to 1.4 mg of niobium/50 ml measured against a solution containing 1.0 mg of niobium/50 ml. Correction graphs to compensate for tantalum and zirconium were prepared at 4500 Å by the procedure described in (b), using solutions containing tantalum up to 10 mg, and solutions containing similar amounts of zirconium; both graphs were linear.

Niobium was then determined in solutions containing major amounts of tantalum. These solutions were prepared by fusing a mixture of the metals in potassium bisulphate and extracting the cooled melts with ammonium oxalate solution. Aliquots were transferred to 50-ml calibrated flasks and treated as described previously; after

correcting for absorption due to tantalum, satisfactory results were obtained. Similar determinations were made using solutions containing major amounts of zirconium. Results of these tests are shown in Table I, Test Nos. 1, 2, 6 and 7.

TABLE I

DETERMINATION OF NIOBIUM IN THE PRESENCE OF ZIRCONIUM OR TANTALUM

Test No.	Zirconium + Niobium (g)	Niobium %	
		Present	Determined
1	0.15	2.1	2.07 2.05
2	0.10	5.1	5.07 4.98
3	0.125	10.7	10.57 10.64
4	0.075	14.7	14.72 14.60
			14.72 14.72
			14.62
5	0.06	20.7	20.70 20.49
Tantalum + Niobium (g)			
6	0.15	2.1	1.96 2.0
7	0.10	5.2	5.19 5.20
8	0.125	10.0	9.89 10.06
9	0.06	20.7	20.87 20.92

Effects of temperature and concentration of reagents

Tests showed that the O. D. of the niobium complex decreased over the range 10 to 30° by 0.007 per degree C rise. In subsequent tests, therefore, solution temperatures were controlled at $20^\circ \pm 1^\circ$ during O. D. measurements. Variation in blank values, over the same temperature range, was negligible. Full development of colour was obtained within 5 min after diluting the solution to the calibration mark, and the colour was stable for at least 90 min. Blank values also remained constant over the same period.

With increase in the amount of alkaline pyrogallol solution (2%), over the range 5 to 15 ml, O. D. increased rapidly, but thereafter, up to 25 ml, the increase in O. D.

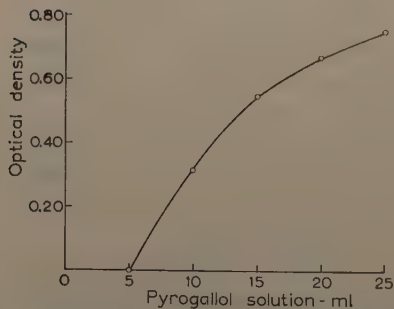


Fig. 3. Effect of alkaline pyrogallol (2%). Niobium 0.5 mg/50 ml; wavelength 4500 Å; cell 2 cm.

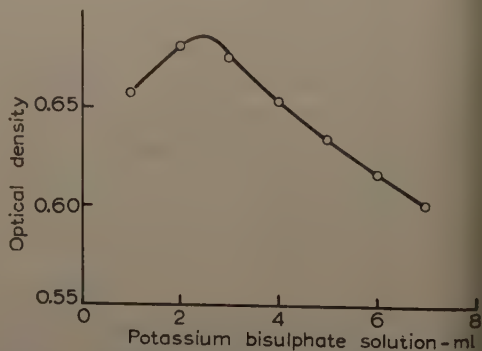


Fig. 4. Effect of potassium bisulphate (10%). Niobium 0.5 mg/50 ml; wavelength 4500 Å; cell 2 cm.

was more gradual. Below 5 ml, the coloured complex was not formed (Fig. 3). The amount of reagent added in subsequent experiments was therefore controlled to $20 \text{ ml} \pm 0.05 \text{ ml}$.

Over the range 1 to 2.5 ml, increase in the amount of potassium bisulphate solution (10%) caused an increase in optical density, but from 2.5 to 7 ml the O. D. decreased (Fig. 4). The amount of solid reagent used for dissolution of the sample must be weighed to within $\pm 50 \text{ mg}$.

Increase in the amount of ammonium oxalate solution (4%) from 5 to 25 ml caused a linear decrease in O. D. and the amount of this reagent, used to prevent hydrolysis, must be weighed to within $\pm 50 \text{ mg}$.

Effect of other metals

In common with many other phenolic compounds, pyrogallol forms coloured complexes with numerous ions. Tests to determine the effects of common alloying constituents and likely impurities showed that, under the conditions used for determining niobium by the recommended method, coloured complexes were formed by copper, iron, molybdenum, tungsten and titanium, in addition to tantalum and zirconium. The extent of interference by these metals is shown in Table II.

TABLE II
EFFECT OF OTHER METALS IN THE DETERMINATION OF NIOBIUM

<i>Metal (1 mg)</i>	<i>Niobium equivalent (mg)</i>
Copper	<0.001
Tin	<0.001
Iron	1.34
Molybdenum	1.20
Tungsten	0.02
Titanium	2.97
Tantalum	0.003
Zirconium	0.001

Interference by tantalum and zirconium was small, and a suitable compensation can be made by using correction graphs, as described earlier. A correction for iron up to about 0.3% can be made, by determining the iron content of the sample (using nitroglycollic acid) and deducting four thirds of the value obtained from the apparent niobium content of the sample. Amounts below about 5% of copper or tin, or 1% of tungsten, had a negligible effect. Interference by molybdenum became significant above about 0.02% but this metal can be separated, as described in the method. Titanium above about 0.01% caused serious interference.

Application of the method

Because of the corrections to be applied in the presence of tantalum, zirconium and possible impurities, the procedure is limited to amounts of niobium above about 2%. The calibration graph is, therefore, applicable over the range 2 to 3%, based on 0.15-g sample, but the method has been extended to the determination of up to about 7% of niobium by using a proportionally smaller sample weight. Experiments

have shown (Table I, Test Nos. 3, 4, 5, 8 and 9) that up to about 20% of niobium can be satisfactorily determined by the recommended differential procedure.

The method was applied to samples of niobium-zirconium alloys containing from 5 to 20% of niobium, and satisfactory results were obtained (Table III).

TABLE III
DETERMINATION OF NIOBIUM IN ZIRCONIUM-NIOBIUM ALLOYS

Sample No.	Niobium %			
	Nominal	Determined		
1	5.0	5.10	5.14	5.07
2	15.0	14.90	14.83	
3	20.0	19.72	19.77	
4 (Zirconium/6.5% Sn/10% Nb)	10.0	8.93	8.99	
		8.96 ^a	8.92 ^a	

^a Tin removed by a preliminary sulphide precipitation

2. DETERMINATION OF TANTALUM IN NIOBIUM AND ZIRCONIUM

Preliminary experiments

Initial tests were made (a) to establish the most suitable wavelength at which to measure absorption of the tantalum-pyrogallol complex in the presence of niobium and zirconium complexes, and (b) using this wavelength, to prepare a calibration graph.

(a) *Absorption curves.* High purity tantalum pentoxide (0.1221 g) was fused with 10 g of potassium bisulphate in a small platinum dish, and the cooled melt was extracted with about 200 ml of hot water containing 20 g of ammonium oxalate. The solution was diluted to 500 ml in a calibrated flask. Then:

1 ml \equiv 0.2 mg of tantalum.

To 7.5 ml of this solution, contained in a 50-ml calibrated flask, 17.5 ml of ammonium oxalate solution (4%) were added, followed by 3.5 ml of potassium bisulphate solution (10%); the total amounts of these reagents in solution were 1.0 and 0.5 g respectively. 5 ml of pyrogallol reagent (15.0% in sulphuric acid (1 + 40)) were added, the solution was diluted to the mark, and set aside for 15 min at 20°. Optical density measurements were made at wavelengths between 3600 Å and 4800 Å, using a Unicam S.P. 60 spectrophotometer and 2-cm cells. The wavelength of maximum absorption of the tantalum complex was found to be at 4000 Å (Fig. 5).

Further absorption curves were prepared as described above, using:

(1) reagents only

(2) 20 ml of niobium solution (1 ml \equiv 1.0 mg of niobium).

Absorption by the niobium complex and the blank were small, and both decreased with increase in wavelength (Fig. 5). The small absorption by the niobium complex at 4000 Å indicated that a correction graph could be used to compensate for amounts of niobium up to about 20 mg.

Further tests showed that solutions containing up to 20 mg of zirconium/50 ml had negligible absorption at 4000 Å under the conditions described above.

(b) *Calibration and correction graphs.* Amounts of tantalum solution (1 ml \equiv 0.2 mg tantalum) ranging from 0 to 7.5 ml were transferred to 50-ml calibrated flasks, and reagents were added in accordance with the procedure described in (a), the weights ammonium oxalate and potassium bisulphate being adjusted as before to 1.0 g

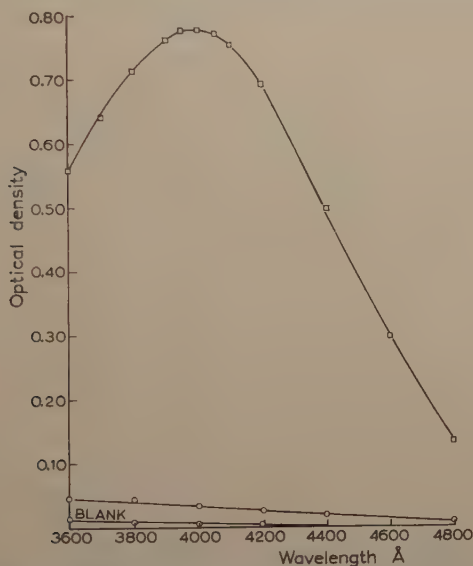


Fig. 5. Absorption curves of tantalum and niobium pyrogallol complexes and "blank" solution (acid medium). Tantalum □ 1.5 mg/50 ml; niobium ○ 20.0 mg/50 ml; cell 2 cm.

and 0.5 g respectively. These solutions were diluted to the mark and optical densities were determined at 4000 Å, using 2-cm cells; a linear calibration graph was obtained. A differential calibration graph was also prepared using solutions containing 1.5 to 20 mg of tantalum/50 ml measured against a solution containing 1.5 mg of tantalum/50 ml.

A correction graph for niobium was prepared at 4000 Å by the procedure described in (b), using solutions containing niobium up to 25 mg; the graph obtained was linear.

TABLE IV

DETERMINATION OF TANTALUM IN THE PRESENCE OF ZIRCONIUM OR NIOBIUM

Test No.	Zirconium + Tantalum (g)	Tantalum %	
		Present	Determined
1	0.15	2.0	1.96 1.95
2	0.25	10.0	10.00 10.00
3	0.15	15.0	15.00 15.00
<i>Niobium + Tantalum</i> (g)			
4	0.15	5.0	4.95 4.95
5	0.25	10.0	9.95 9.88
6	0.15	14.8	14.80 15.00
7	0.15	20.0	19.92

Tantalum was then determined in solutions containing major amounts of niobium and, after correcting for absorption due to niobium, satisfactory results were obtained. Similar tests, in the presence of major amounts of zirconium, also gave satisfactory results (Table IV, Test Nos. 1 and 4).

Effects of temperature and concentration of reagents

The optical density of the tantalum complex decreased over the range 10 to 30° by 0.0085 per degree C rise. In subsequent tests, therefore, solution temperatures were controlled at $20^\circ \pm 1^\circ$ during optical density measurements. Variation in blank values over the same temperature range, was negligible. Full development of colour was obtained within 5 min after diluting the solution to the calibration mark, and the colour was stable for at least 90 min. Blank values also remained constant over the same period.

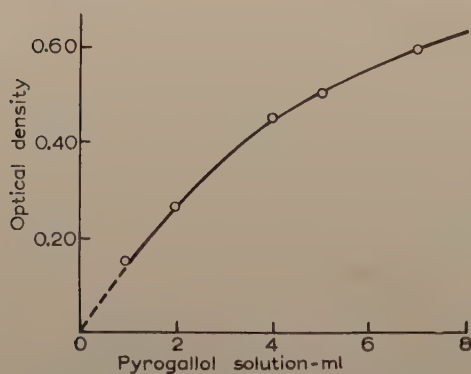


Fig. 6. Effect of acid pyrogallol (15%). Tantalum 1.0 mg/50 ml; wavelength 4000 Å; cell 2 cm.

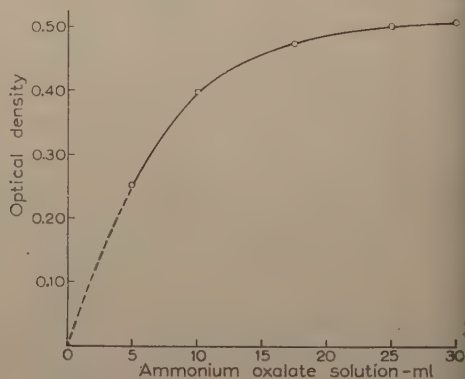


Fig. 7. Effect of ammonium oxalate (4%). Tantalum 1.0 mg/50 ml; wavelength 4000 Å; cell 2 cm.

With increase in the amount of acid pyrogallol solution (15%), up to 7 ml (Fig. 6) there was an increase in the optical density of the complex. The amount of reagent added in subsequent tests was controlled at $5 \text{ ml} \pm 0.05 \text{ ml}$.

Over the range 1 to 9 ml, increase in the amount of potassium bisulphate (10%) caused a linear increase in optical density. The amount of solid reagent used for dissolution of the sample must be weighed to within $\pm 50 \text{ mg}$.

Increase in the amount of ammonium oxalate solution (4%) from 2 to 10 ml caused a sharp increase in optical density; from 10 to 30 ml the increase was more gradual, (Fig. 7). The amount used, to prevent hydrolysis, must be weighed to within $\pm 50 \text{ mg}$.

Effects of other metals

Tests to determine the effects of common alloying constituents and likely impurities showed that, under the conditions for determining tantalum by the recommended method, coloured complexes were formed by copper, iron, molybdenum, tungsten and titanium, in addition to niobium. The extent of interference by these metals is shown in Table V. No interference was caused by zirconium up to at least 98%. Interference by niobium was small and a suitable compensation can be made using a correction

graph, as described earlier. A correction for iron, up to about 1.0% can be made by determining the iron content of the sample, using thioglycolic acid, and subtracting one fifth of the value obtained from the apparent tantalum content of the sample. Amounts up to about 5% of copper, aluminium or nickel, or 0.2% of tungsten had no significant effect. Interference by molybdenum became significant above about 0.05%, but this metal can be separated, as described in the method. Titanium above about 0.01% caused serious interference.

TABLE V
EFFECTS OF OTHER METALS IN THE
DETERMINATION OF TANTALUM

<i>Metal</i> (1 mg)	<i>Tantalum equivalent</i> (mg)
Copper	0.004
Iron	0.18
Aluminium	<0.001
Nickel	0.003
Molybdenum	0.33
Tungsten	0.08
Titanium	3.84
Niobium	0.004

Application of the method

Determination of tantalum by the direct procedure is limited to amounts above about 2%, and the useful range of the calibration graph is from about 2 to 7%, based on a 0.15-g sample. Tests have shown (Table IV, Test Nos. 2, 3, 5 to 7) that amounts up to about 20% of tantalum can be satisfactorily determined by the recommended differential procedure.

The method was applied to samples of niobium-tantalum alloys containing 15 to 30% of tantalum, and satisfactory results were obtained (Table VI).

TABLE VI
DETERMINATION OF TANTALUM IN ZIRCONIUM-TANTALUM
AND NIOBIUM-TANTALUM ALLOYS

<i>Sample No.</i>	<i>Tantalum %</i>	
	<i>Nominal</i>	<i>Determined</i>
1 (Niobium/15%Ta/5%Mo alloy)	15.0	15.20 15.05
2 (Niobium/15%Ta/5%Mo alloy)	15.0	15.1 15.3
3 Zirconium/Ta alloy	27-28	27.9 27.9 28.0 28.0.

METHODS

I. DETERMINATION OF NIOBIUM IN ZIRCONIUM AND TANTALUM

Special reagents

Ammonium oxalate solution (4%). Dissolve 40.0 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in about 900 ml of warm water, cool and dilute to 1 l.

Potassium bisulphate solution (10%).

Sodium sulphite solution (20%). Dissolve 50 g of $\text{Na}_2\text{SO}_3 \cdot 7 \text{H}_2\text{O}$ in about 150 ml of water and dilute to 250 ml. Prepare this solution immediately before use.

Alkaline pyrogallol solution (2.0%). Dissolve 2.0 g of pyrogallol in about 40 ml of sodium sulphite solution (20%), then filter through a No. 40 Whatman paper into a dry, 100-ml calibrated flask. Wash the paper with sufficient sodium sulphite solution to dilute the filtrate to 100 ml.

Standard niobium solution. Calcine about 0.1 g of high-purity niobium pentoxide at 850° , for 30 min. Cool, transfer 71.5 mg of the calcined oxide to a small platinum dish and fuse with 10.0 g of potassium bisulphate. Cool, transfer the dish and contents to a beaker (400 ml) and extract with a hot solution of 20.0 g of ammonium oxalate in about 250 ml of water. Heat gently until the melt has dissolved, then transfer the cooled solution to a 500-ml calibrated flask and dilute to the mark.

1 ml \equiv 0.1 mg of niobium.

Standard zirconium solution. Fuse 80 mg of iodide-zirconium with 2.0 g of potassium bisulphate in a conical flask (100 ml). Cool, extract with a hot solution of 3.2 g of ammonium oxalate in about 60 ml of water. Heat gently until the melt has dissolved, then transfer the cooled solution to a 100-ml calibrated flask and dilute to the mark.

1 ml \equiv 0.8 mg of zirconium

Standard tantalum solution. Fuse 0.122 g of high purity tantalum pentoxide with 2.0 g of potassium bisulphate in a conical flask (100 ml). Cool, extract with a hot solution of 4.0 g of ammonium oxalate in about 60 ml of water and continue as described for preparation of the zirconium solution, then:

1 ml \equiv 1.0 mg of tantalum.

Preparation of calibration graphs

Graph 1. For niobium content 2–7 %. Add, separately, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of the standard niobium solution (1 ml \equiv 0.1 mg Nb) to five 50-ml calibrated flasks. Add to each, and a blank, sufficient ammonium oxalate solution (4%) and potassium bisulphate solution (10%) to bring the volumes of these reagents to 20.0 ml and 5.0 ml respectively. Thus:

Standard niobium solution, ml	Ammonium oxalate solution, ml	Potassium bisulphate solution, ml
1.0	19.0	4.8
2.0	18.0	4.6
3.0	17.0	4.4
4.0	16.0	4.2
5.0	15.0	4.0
NIL	20.0	5.0

Add to each, 20.0 ml of alkaline pyrogallol solution (2%), dilute to the mark and allow to stand for 15 min at $20^\circ \pm 1^\circ$. Measure the optical densities at a wavelength of 4500 Å, using 2-cm cells.

Graph 2. For niobium content 7–20%. Prepare these solutions simultaneously with the sample solution(s).

Add, separately, 10.0, 11.0, 12.0, 13.0 and 14.0 ml of the standard niobium solution (1 ml \equiv 0.1 mg Nb) to five 50-ml calibrated flasks. Add ammonium oxalate solution (4%) and potassium bisulphate solution (10%) to bring the total volume of these reagents to 20.0 ml and 5.0 ml respectively. Add 20.0 ml of the alkaline pyrogallol solution (2%), dilute to the mark and allow to stand for 15 min at $20^\circ \pm 1^\circ$. Use these solutions at the appropriate stage in the differential procedure 2.

Preparation of correction graphs

(a) *For zirconium.* Add, separately, 5.0, 12.5, 17.5, and 25.0 ml of the standard

zirconium solution (1 ml \equiv 0.8 mg Zr) to four 50-ml calibrated flasks, and continue as described for preparation of calibration Graph 1.

(b) *For tantalum.* Add, separately, 5.0, 10.0, 15.0 and 20.0 ml of the standard tantalum solution (1 ml \equiv 1.0 mg Ta) to four 50-ml calibrated flasks and continue as described in (a).

Procedure 1. For niobium content 2–7%. Make a reagent blank determination and check at least two points on the calibration graph with each batch of samples.

Transfer a suitable weight of sample (Note 1) to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and heat over a Bunsen flame until the sample has dissolved (Note 2). Cool, extract, with a hot solution of 8.0 g of ammonium oxalate in about 60 ml of water; heat gently until the melt has dissolved. Cool (crystals will separate at this stage) and wash the solution into a 250-ml calibrated flask; shake to dissolve any crystals and dilute to the mark. Transfer a 25-ml aliquot to a 50-ml calibrated flask, add 20.0 ml of alkaline pyrogallol solution (2.0%) and dilute to the mark. Allow to stand for 15 min at $20^\circ \pm 1^\circ$ and measure the optical density at 4500 Å, using 2-cm cells. Correct for absorption due to zirconium and/or tantalum and calculate the niobium content of the sample, using the calibration graph.

Procedure 2. For niobium content 7–20%. Transfer a suitable weight of sample (Note 3) to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and prepare the solutions for optical density measurement, as described in Procedure 1.

Rinse out two 2-cm cells marked "reference" and "test", once with water, twice with ethyl alcohol then once with ether. Allow the cells to drain, then polish the exterior surfaces with chamois leather.

To determine the cell blank, fill both cells with the 10.0-ml "reference" solution prepared for Graph 2, and measure the optical density with respect to each other at wavelength of 4500 Å. Correct for this cell blank in all subsequent optical density measurements. Fill the "test" cell successively with the remaining calibration solutions, then with the sample solution(s). In each instance, determine the O. D. against the 10.0-ml "reference" solution. Prepare a graph relating O. D. to mg niobium/50 ml, correct for absorption due to zirconium and/or tantalum in the sample, and calculate the niobium content.

A calibration graph must be prepared with each batch of samples.

Notes

1. In order to facilitate fusion, the sample must be finely divided.

Suitable sample weights are as follows:

Nb(%)	Sample weight (g)
2–3	0.15
4–6	0.10
6–7	0.07

For samples which are difficult to dissolve in bisulphate proceed as follows:

Transfer the sample to a small platinum dish, add 10 ml of water and 1 ml of conc. nitric acid ($d = 1.42$) then heat gently and add hydrofluoric acid, dropwise. Evaporate the solution to

dryness, calcine at 800° for about 10 min, fuse the oxides with 5.0 g of potassium bisulphate, then follow the recommended procedure.

2. To correct for the effect of iron, up to about 0.3%, determine the iron content of the sample, using thioglycolic acid, and deduct four thirds of the value obtained, from the apparent niobium content.

Molybdenum, above about 0.02%, interferes, but can be separated as follows:

Fuse the sample in potassium bisulphate and digest the cold melt with hot water for about 15 min. Cool, add 30 ml of ammonium hydroxide ($d = 0.925$), heat to boiling and maintain just below the boiling point for 15 min. Filter through a paper pulp pad, wash with a hot solution of ammonium hydroxide (1 + 50) containing about 5 g of ammonium nitrate/100 ml. Dry, char and finally calcine the precipitate at 800° . Fuse the oxides with 5.0 g of potassium bisulphate and continue as described in the procedure.

3.

Suitable sample weights are as follows:

Nb(%)	Sample weight (g)
7-9	0.15
10-11	0.125
12-14	0.10
15-18	0.075
20	0.060

2. DETERMINATION OF TANTALUM IN ZIRCONIUM AND NIOBIUM

Special reagents

Acid pyrogallol solution (15%). Dissolve 15.0 g of pyrogallol in about 60 ml of water and 5.0 ml of sulphuric acid (1 + 1). Transfer the solution to a 100-ml calibrated flask and dilute to the mark. Filter through a No. 40 Whatman paper before use.

Standard tantalum solution. Calcine about 0.15 g of high-purity tantalum pentoxide at 850° for 30 min. Cool, transfer 0.1221 g of the calcined oxide to a small platinum dish and fuse with 10.0 g of potassium bisulphate. Cool, transfer the dish and contents to a beaker (400 ml) and extract with a hot solution of 20.0 g of ammonium oxalate in about 250 ml of water. Heat gently until the melt has dissolved, then transfer the cooled solution to a 500-ml calibrated flask and dilute to the mark.

1 ml \equiv 0.2 mg of tantalum.

Standard niobium solution. Fuse 0.143 g of high-purity niobium pentoxide with 2.0 g of potassium bisulphate in a conical flask (100 ml). Cool, extract with a hot solution of 4.0 g of ammonium oxalate in about 60 ml of water. Heat gently until the melt has dissolved, then transfer to a 100 ml calibrated flask and dilute to the mark.

1 ml \equiv 1.0 mg of niobium.

Preparation of calibration graphs

Graph 1. For tantalum content 2-7%. Add, separately, 2.0, 4.0, 6.0 and 7.5 ml of the standard tantalum solution (1 ml = 0.2 mg Ta) to four 50-ml calibrated flasks. Add to each, and a blank, sufficient ammonium oxalate solution (4%) and potassium bisulphate solution (10%) to bring the volumes of these reagents to 25.0 ml and 5.0 ml respectively. Thus:

Standard tantalum solution, ml	Ammonium oxalate solution, ml	Potassium bisulphate solution, ml
2.0	23.0	4.6
4.0	21.0	4.2
6.0	19.0	3.8
7.5	17.5	3.5
NIL	25.0	5.0

Add to each, 5.0 ml of the acid pyrogallol solution (15%), dilute to the calibration mark and allow to stand for 15 min at $20^{\circ} \pm 1^{\circ}$. Measure the optical densities at a wavelength of 4000 Å, using 2-cm cells.

Graph 2. For tantalum content 7–20%. Prepare these solutions simultaneously with the sample solution(s).

Add, separately, 7.5, 10.0, 12.5 and 15.0 ml of the standard tantalum solution (1 ml \equiv 0.2 mg Ta) to four 50-ml calibrated flasks. Add ammonium oxalate solution (10%) and potassium bisulphate solution (10%) to bring the total volumes of these reagents to 25.0 ml and 5.0 ml respectively. Add 5.0 ml of the acid pyrogallol solution (15%), dilute to the mark and allow to stand for 15 min at $20^{\circ} \pm 1^{\circ}$. Use these solutions at the appropriate stage in the differential procedure 2.

Preparation of correction graph for niobium

Add, separately, 5.0, 12.5, 17.5 and 25.0 ml of the standard niobium solution (1 ml \equiv 1.0 mg Nb) to four 50 ml calibrated flasks and continue as described for preparation of calibration Graph 1.

Procedure 1. For tantalum content 2–7%. Make a reagent blank determination and check at least two points on the calibration graph with each batch of samples.

Transfer 0.15 g of the sample to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and heat over a Bunsen flame until the sample has dissolved (Note 1). Cool, extract with a hot solution of 10.0 g of ammonium oxalate in about 60 ml of water; heat gently until the melt has dissolved. Cool, transfer the solution to a 250-ml calibrated flask and dilute to the mark. Transfer a 25-ml aliquot to a 50-ml calibrated flask, add 5.0 ml of acid pyrogallol solution (15%) and dilute to the mark. Allow to stand for 15 min at $20^{\circ} \pm 1^{\circ}$ and measure the O. D. at 4000 Å, using 2-cm cells. If niobium is present, correct for absorption due to the niobium-pyrogallol complex and calculate the tantalum content of the sample, using the calibration graph.

Procedure 2. For tantalum content 7–20%. Transfer 0.15 g of the sample (Note 2) to a dry conical flask (100 ml), add 5.0 g of potassium bisulphate and prepare the solutions for O. D. measurement, as described in Procedure 1.

Prepare two 2-cm cells marked “reference” and “test” as described for the differential absorptiometric determination of niobium. To determine the cell blank, fill both cells with the 7.5-ml tantalum “reference” solution prepared for Graph 2 and measure the O. D. with respect to each other at a wavelength of 4000 Å. Correct for the cell blank in all subsequent O. D. measurements.

Fill the “test” cell successively with the remaining calibration solutions and finally with the sample solution(s). In each instance, determine the O. D. against the 7.5-ml “reference” solution. Prepare a calibration graph relating O. D. to mg tantalum/50 ml, correct for absorption due to niobium in the sample and calculate the tantalum content.

A calibration graph should be prepared with each batch of samples.

Notes

1. The sample must be finely divided. For samples which are difficult to dissolve, use the procedure described in Note 1, p. 131, for the *Determination of niobium in zirconium and tantalum*.
2. For samples containing 7–10% of tantalum, use 0.25 g of sample, dissolve as described in Note 1, p. 131.

To correct for the effect of iron, up to about 1.0%, determine the iron content of the sample, using thioglycolic acid and deduct one fifth of the value obtained from the apparent tantalum content. Molybdenum above about 0.05% interferes but can be separated as described in Note 2, p. 132.

CONCLUSIONS

The direct absorptiometric procedure using alkaline pyrogallol solution is suitable for determining niobium over the range 2 to 7% in zirconium and tantalum. The method can be extended to the determination of larger amounts of niobium, by using a differential procedure. Corrections must be applied for zirconium, tantalum or impurity amounts of iron. Amounts up to 5% of copper or 1% of tungsten have a negligible effect. Titanium above about 0.01% causes significant interference.

The procedure based on the use of acid pyrogallol solution is suitable for determining tantalum over the range 2 to 7% in zirconium and niobium. The differential procedure is recommended for determining larger amounts of tantalum. In the presence of niobium or impurity amounts of iron, a correction must be applied. Zirconium does not interfere. Amounts up to about 5% of copper, aluminium or nickel, or 0.2% of tungsten have a negligible effect. Titanium above about 0.01% causes serious interference. The effect of molybdenum can be overcome by making a preliminary separation of tantalum (or niobium) with ammonium hydroxide.

In the determination of niobium or tantalum up to about 5%, the precision of the method is of the order $\pm 0.05\%$.

About 12 determinations can be made in a normal working day by one analyst.

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SUMMARY

Recent developments in the metallurgy of niobium, tantalum and zirconium have necessitated provision of analytical procedures for determining niobium and tantalum in the presence of each other and in the presence of zirconium. For this purpose, absorptiometric procedures based on the formation of yellow coloured complexes, between pyrogallol and niobium or tantalum, have been critically examined. Direct absorptiometric procedures are described, which are suitable for determining niobium or tantalum in the range 2 to 7%; when either of these metals exceeds 7%, differential absorptiometric procedures are recommended. Corrections must be made for absorption due to the presence of other metals which form complexes with pyrogallol. In the determination of niobium or tantalum up to 5%, the precision of the method is about $\pm 0.05\%$. About 12 determinations can be made in a day, by one analyst.

RÉSUMÉ

Après une étude critique, des méthodes absorptiométriques rapides sont proposées pour le dosage du niobium, en présence de tantale et de zirconium et pour le dosage du tantale, en présence de niobium et de zirconium. Ces procédés sont basés sur la formation de complexes jaunes de ces éléments avec le pyrogallol. Des corrections doivent être faites en présence d'autres métaux formant des complexes avec ce réactif.

ZUSAMMENFASSUNG

Es werden „absorptiometrische“ Methoden beschrieben zur raschen Bestimmung von Niob in Gegenwart von Tantal und Zirkonium sowie für Tantal in Gegenwart der beiden anderen Metalle. Die Grundlage der Methode beruht auf der Komplexbildung dieser Metalle mit Pyrogallol. Sind ausserdem noch andere Metalle vorhanden, die mit Pyrogallol Komplexe bilden, muss ein Korrektionsfaktor angewandt werden.

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HIGHLY ACCURATE AND PRECISE METHOD FOR THE ASSAY OF CHROMIUM METAL AND CHROMIUM(III) OXIDE

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Because the magnitude of ordinary analytical errors is too high to provide the desired accuracy with precision, the direct assay of high purity materials is often avoided in favor of the determination of suspected minor contaminants. The usual practice of estimating the purity of such materials by difference after quantitative spectrographic analysis provides only an incomplete assay because several common impurities, such as oxygen, nitrogen, sulfur, and the halogens, are not readily amenable to spectrographic measurement.

In the case of high-purity chromium metal and chromium(III) oxide, a direct assay method has been developed which is suitable for routine use and capable of an accuracy and precision well within one part in a thousand. The procedure employs the addition of a weighed excess of solid ferrous ammonium sulfate hexahydrate to a sample solution which has been oxidized to the hexavalent state. The excess ferrous is then measured by amperometric titration¹. Although a previous study² indicated that reagent-grade Mohr's salt can be obtained commercially which possesses a reducing power which is 99.8% of its theoretical strength, the optimum accuracy is assured by a preliminary assay of the ferrous ammonium sulfate hexahydrate against primary-standard-grade potassium dichromate using the same amperometric procedure.

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In order to check the accuracy of results obtained using Mohr's salt, the purity of the chromium metal employed was determined using primary-standard arsenic trioxide as reductant. Excess arsenite was measured by potentiometric titration. Comparison with respect to accuracy and precision indicated that either method could be used. However, with respect to operational simplicity, the Mohr's-salt reductant used in conjunction with the amperometric titration, was much to be preferred.

EXPERIMENTAL

Apparatus

The equipment used in the amperometric titration has been previously described in the study made of the purity of Mohr's salt².

A Leeds and Northrup A.C. Operated pH Indicator (7664-Al), in conjunction with the appropriate platinum electrode and calomel reference electrode, was used to perform the potentiometric titrations where comparison was made with the arsenic trioxide method.

Reagents and solutions

The primary standards, potassium dichromate and arsenic trioxide, were obtained from the Mallinckrodt Chemical Works.

The ferrous ammonium sulfate hexahydrate was also supplied by Mallinckrodt (Analytical Reagent #5068). Assay against primary-standard dichromate indicated its reducing strength to be $99.87\% \pm 0.022$ of the theoretical value².

The 0.0200 *N* solution of potassium dichromate was prepared directly from the primary standard material.

A 0.05 *N* solution of ceric ammonium sulfate was prepared from the dihydrate, and standardized against primary-standard arsenic trioxide using osmium tetroxide as catalyst³.

All other chemicals used were of reagent-grade quality. These, or the solutions prepared from them, include: ammonium persulfate, sulfuric acid 96%, perchloric acid 72%, sulfuric acid 1 : 1, nitric acid 1 : 1, sulfuric acid 3 *N*, sodium hydroxide 3 *N*, silver nitrate solution 5%, osmium tetroxide solution 0.01 *M* in 0.1 *M* sulfuric acid.

Procedure for the dissolution of samples and oxidation of chromium to the hexavalent state

Approximately 0.5 g of chromium metal, accurately weighed to the nearest 0.1 mg, was dissolved by heating gently with 30 ml of sulfuric acid, 1 : 1, in a 600-ml beaker. Either powdered metal, or larger pieces, dissolved readily in this reagent after a short induction period. The induction period can be avoided by "grinding" the pieces with a stirring rod to initiate the reaction. After complete dissolution, the solution was brought to a volume of about 250 ml with distilled water.

The chromium(III) oxide samples were converted to chromic acid by the action of hot concentrated perchloric acid⁴. An accurately weighed sample of approximately 0.5 g was placed in a dry 600-ml beaker, and covered with 20 ml of a 1 : 1 mixture of perchloric acid (72%) and concentrated sulfuric acid. After heating for about 20 min at the fuming point, the sample was completely oxidized to chromic acid; and after cooling, the chromic acid was dissolved in about 250 ml of distilled water.

Subsequently, sample solutions prepared from either the metal or the oxide were treated with ammonium persulfate to effect complete oxidation to dichromate. In accord with the recommendations of HILLEBRAND *et al.*⁵, 6 ml of nitric acid, 1 : 1, were added, and the solutions brought to a boil before the addition of 10 ml of the silver nitrate solution (5%). After boiling resumed, ammonium persulfate was added cautiously from a scoop as the solid reagent, in portions each weighing 1–2 g. Repeated additions, after intervals of boiling, were required to completely oxidize the chromium at these high concentrations. The addition of ammonium persulfate in solution form was found to be impractical, and often led to incomplete oxidation.

which was difficult to observe visually. Solid reagent can be added in considerable excess (as much as 15 g) without adversely increasing the volume of the solution. In the case of the samples of chromium(III) oxide, a lesser amount of persulfate was required because chromium was partially oxidized by the perchloric acid treatment used for dissolution. After the last addition of persulfate, the solutions were boiled for 10 min to destroy excess persulfate. Hydrochloric acid can be added at this point to reduce manganese if its presence is suspected.

Procedure for the amperometric titration of the oxidized sample solutions

Titration of the oxidized solutions was accomplished in the same manner as described in the assay of Mohr's salt against primary-standard potassium dichromate². Based upon a preliminary calculation of the dichromate resulting from the oxidation of the sample (assuming 100% purity), solid ferrous ammonium sulfate hexahydrate was weighed accurately to the nearest milligram to provide an equivalent amount of reductant plus a 50 mg excess. The assayed strength of the Mohr's salt was used as a correction factor before this weighing. The weighed crystals were added directly to the cooled dichromate solution, and were dissolved by stirring magnetically, in approximately 5 min. Excess of ferrous ion was indicated by an anodic current at -1.0 V applied to the rotating platinum electrode *vs.* S.C.E. and was titrated amperometrically using the 0.0200 *N* solution of potassium dichromate. The purity of the sample was calculated using the appropriate mequiv. weight from the net number of mequivs. of ferrous ammonium sulfate consumed by the oxidized sample solution.

Procedure for the titration of oxidized solutions using arsenic trioxide and a potentiometric end-point

In the comparison method, where arsenic trioxide was used as the reductant, a calculated amount of primary-standard-grade solid arsenic trioxide was weighed to provide an excess of about 0.2 mequivs. greater than the equivs. of chromium to be measured. Using extreme care to prevent loss of arsenic trioxide, the weighed oxide was transferred to a covered 150-ml beaker and dissolved by the addition of 10 ml of 3 *N* sodium hydroxide. The caustic arsenite solution was then neutralized with 3 *N* sulfuric acid. Reduction of either a solution of an exact weight of potassium dichromate or of an oxidized sample was accomplished by the addition of the neutralized arsenite solution. After stirring magnetically for 15 min, the excess arsenite was titrated potentiometrically, (calomel *vs.* anodized platinum electrodes), with 0.05 *N* ceric ammonium sulfate in the presence of 3 drops of 0.01 *M* osmium tetroxide catalyst. The platinum electrode used for the potentiometric titrations was anodized by making it the anode in 5% sulfuric acid for 15 sec with an applied voltage of 4 V.

RESULTS

Twelve replicate determinations of high purity chromium metal are listed in Table I along with the average purity of the metal and the 99% confidence limits of this average. The precision of the determination was estimated from the standard deviation to be about 3 parts in ten thousand with a 99% upper confidence limit of about 4 parts in ten thousand. This variability was in excellent agreement with that obtained using primary-standard potassium dichromate².

Table II shows the results of four replicate determinations of two samples of chromium trioxide. In the case of sample A the estimate of the standard deviation was in good agreement with that previously found. However, because a fewer number of replicates were taken, the confidence limits necessarily are less rigorous. In the case of sample B the standard deviation was twofold greater than that previously obtained. It is obvious that the first result listed for this sample is influencing this estimate of precision and therefore less confidence can be placed upon the average if this datum is included. However, because no obvious reason for rejecting this result was noted, other than variable sampling technique, it has been included in Table II.

Preliminary work with arsenic trioxide, as a primary standard reductant for dichromate, was carried out on solutions of primary standard potassium dichromate where such variables as the condition of the platinum electrode and the influence

TABLE I
ASSAY (IN %) OF HIGH PURITY CHROMIUM USING STANDARDIZED
SOLID FERROUS AMMONIUM SULFATE HEXAHYDRATE

Grams chromium		% purity
taken	found	
0.5387	0.53875	100.01
0.4811	0.48065	99.92
0.4960	0.49596	99.99
0.5619	0.56177	99.98
0.5427	0.54263	99.99
0.4810	0.48084	99.97
0.5321	0.53180	99.94
0.5825	0.58232	99.97
0.4874	0.48740	100.00
0.3787	0.37844	99.93
0.4933	0.49319	99.98
0.4737	0.47353	99.96
Average		99.970
99% Confidence limits of average		99.945-99.995
Standard deviation of an individual measurement		± 0.028 ($N = 12$)
99% Upper confidence limit of the standard deviation		0.053

of silver nitrate was investigated. Table III summarizes the finding of this study where results are calculated in terms of the purity of the potassium dichromate assuming 100.00% purity for arsenic trioxide. The need to anodize the platinum electrode was evident from the shape of potentiometric titration curves which were skewed when no prior anodizing was performed. Accordingly, the first two results reported were slightly higher than those found when the electrode was anodized. The effect of silver nitrate, although not rigorously evaluated, appears to have a slight influence causing a bias toward a higher result as indicated by the last two data in Table III.

TABLE II
PURITY OF CHROMIUM TRIOXIDE SAMPLES

	% Purity Cr_2O_3	
	Sample A	Sample B
	99.00	99.11
	99.10	99.41
	99.00	99.32
	90.06	99.32
Average	99.04	99.29
95% Confidence limits of average	98.95-99.13	99.08-99.50
Standard deviation ^a of an individual measurement	± 0.055	0.13
95% Upper confidence limit of the standard deviation	0.16	0.38

^a $N = 4$

TABLE III
THE COMPARISON OF PRIMARY-STANDARD ARSENIC TRIOXIDE^a
versus PRIMARY-STANDARD POTASSIUM DICHROMATE^b BY
POTENTIOMETRIC TITRATION

Grams $K_2Cr_2O_7$		% purity $K_2Cr_2O_7$
taken	found	
1.4082	1.4100	100.13 ^e
1.4174	1.4193	100.13 ^c
1.4137	1.4142	100.04 ^d
1.4010	1.4012	100.02 ^d
1.4172	1.4182	100.07 ^e
1.4189	1.4197	100.06 ^e

^a Obtained from Mallinckrodt Chemical Works. Reported assay on label 99.95-100.05% As_2O_3 .

^b Obtained from Mallinckrodt Chemical Works. Reported assay on label 99.95-100.05% $K_2Cr_2O_7$.

^c Electrodes were not anodized between titrations and silver was not added to the solution.

^d Electrodes were anodized, silver was not added to the solution.

^e Electrodes were anodized, silver added to the solution.

TABLE IV
ASSAY OF HIGH PURITY CHROMIUM
USING ARSENIC OXIDE^a AS REDUCTANT

Grams chromium		% purity
taken	found	
0.6471	0.64734	100.04
0.5366	0.53671	100.02
Average = 100.03 ^b		

^a Assay of arsenic oxide calculated from data in Table III was 99.95% As_2O_3 assuming primary-standard potassium dichromate to be 100.00%.

^b Compare with value of 99.970% shown in Table I.

Table IV shows duplicate results by the arsenic trioxide method for the analysis of the chromium metal previously assayed using ferrous ammonium sulfate. In order to facilitate comparison with the result previously shown in Table I, where potassium dichromate was the primary-standard reference material, the purity of the arsenic trioxide was calculated as 99.95% from the data in Table III (excluding the first two data). The agreement between methods (99.97% vs. 100.03%) was well within the desired accuracy and precision.

DISCUSSION AND CONCLUSIONS

Excellent results were obtained in the analysis of chromium by the use of solid, ferrous ammonium sulfate hexahydrate as a reductant in conjunction with an amperometric end-point. The accuracy and precision of the method were shown to be well within one part per thousand.

Reliable results were also obtained using the arsenic trioxide method. However, it possesses inherently a number of slow steps. These include the precautions which one must take in weighing the oxide (because of its comparatively low gravimetric factor), dissolving it prior to addition to the dichromate, and the subsequent potentiometric end-point, which must be estimated by dropwise additions of ceric ammonium sulfate. In addition, the platinum electrode should be anodized before each titration. By comparison, the amperometric end-point is considerably more rapid where only 6 additions of titrant provide a suitable end-point.

SUMMARY

A method capable of a precision of 3 to 5 parts in ten thousand has been developed for the routine assay of high purity chromium metal and chromium trioxide. Use has been made of the favorable gravimetric factor of ferrous ammonium sulfate and of an amperometric end-point. Comparison with the arsenic trioxide method was made.

RÉSUMÉ

Une méthode est proposée pour l'analyse du chrome métallique très pur et de l'oxyde de chrome(III). On utilise comme réactif le sulfate double de fer(II) et d'ammonium hexahydraté dont on détermine l'excès par titrage ampérométrique.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Analyse von sehr reinem Chrommetall und Chrom-(3)-oxyd mit Eisen-(2)-Ammoniumsulfat-hexahydrat, dessen Überschuss durch ampérometrische Titration bestimmt wird.

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A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES

V. A SIMPLIFIED SCHEME FOR THE DETECTION OF ALL TYPES OF INSOLUBLE SUBSTANCES

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In the previous papers¹ of this series it has been shown that a large number of compounds become almost insoluble in acids after being heated at a high temperature for 2-9 h and thus must be categorized as 'insoluble substances'. An important problem to be considered is the detection of these compounds in qualitative analysis. The previous method of detecting the insoluble substances (which has been dealt with in two earlier papers^{2,3}) is convenient when the number of such substances is comparatively small and limited. With the addition of a very large number of substances to this category — and the number of such substances is likely to be continuously increased — it is necessary that a scheme be devised which has a universal character and can provide for the detection of all types of insoluble substances that have already been added or may be added in the future.

As the provided increase in the number of insoluble substances is likely to make the scheme for their detection more and more complicated, it has been found necessary to combine this scheme with the schemes used for the detection of anions⁴ as well as of cations⁵. In this way many of the insoluble substances are removed and form part both of the sodium carbonate filtrate used in the detection of anions and the acid solution used for the detection of cations.

Further simplification of the scheme for the detection of the insoluble substances is possible by taking the product of fusion with $\text{KOH} + \text{K}_2\text{CO}_3 + \text{KNO}_3$, dividing the large number of basic radicals present in it into different groups with various reagents and combining these groups with the corresponding groups obtained in the main scheme for the basic radicals⁵. In this way duplication of work and waste of time is avoided in the systematic analysis of two separate solutions containing practically the same elements. The manner in which the product of fusion with $\text{KOH} + \text{K}_2\text{CO}_3 + \text{KNO}_3$ is divided into different groups by various reagents and the solutions thus obtained are combined with the corresponding groups of the systematic scheme for the basic radicals is shown in Tables I and II.

The new scheme which is meant to provide for all types of insoluble substances will be seen to differ from the previous scheme^{2,3} in the following ways:

(1) The mixture is treated first with sodium carbonate solution to remove the large majority of anions. This also removes a number of substances which otherwise might have formed part of the insoluble residue; *e.g.* ferrocyanides, ferricyanides, nitrotrussides (form ferrocyanides), sulphates of lead and strontium, manganese phosphate and the oxides of molybdenum and tungsten. For instance, a substance like SrSO_4

TABLE I

Boil 2-3 g of the mixture with 8-10 g of sodium carbonate (AnalaR quality) in about 100 ml of water for 10 min. Filter.		
Residue: Hydroxides of Th, Cr, Fe, Cu, Co, Ni, Mn, $\text{Na}_2\text{U}_2\text{O}_7$; carbonates of Pb, Ba, Sr, Ca etc. and other soluble and insoluble contents of the mixture. Subject it to the acid treatments (Procedure I) ⁵ ; take up with dil. HCl, filter and wash with hot water.		Filtrate: Almost all the anions and certain basic radicals.
Residue: The following insoluble compounds will be present in addition to all the insoluble substances for alkaline fusion mentioned in a previous paper ³ ($-\text{SrSO}_4 + \text{CrCl}_3$) ^a . Phosphate of Cr; Arsenates of Zr, Ti, Cr and Sn; Antimonates of Cu, Zn, Cd, Mn, Co, Ni, Mg, Cr, Be, Ca, Sr, Ba, Al, Th, Zr and U; Chromites of Be, Mg, Zn, Cd, Cu, Co, Ni, Mn, Zr, Ce and U; Aluminates of Cu, Zn, Co, Ni and Mn; Tungstates of Cu, Co, Ni, Zn, Cr and Zr; Tellurates of Cr and Zr; Vanadates of Cr and Zr; Chloride of Ag; and H_2WO_4 derived from the insoluble tungstates and tungsten metal. Treat with NH_4OH solution and filter.	Filtrate: All the basic radicals.	Analyse according to the scheme for anions ⁴ .
Residue: All the above mentioned compounds with the exception of AgCl and H_2WO_4 . Fuse with a large excess of a fusion mixture consisting of $\text{KOH} + \text{K}_2\text{CO}_3 + \text{KNO}_3$ in a nickel crucible over a blow-pipe flame.	Filtrate: Ammonium tungstate and silver-ammonia complex.	Analyse according to the scheme for basic radicals ⁵ .
The following reactions take place:		
Test for W and Ag in usual fashion.		

	Zirconium tellurate	
Zinc chromite	$\rightarrow K_2CrO_4 + K_2ZnO_2$	$K_2ZnO_2 + K_3SbO_4 \leftarrow$ Zinc antimonate
Beryllium chromite	$\rightarrow K_2CrO_4 + K_2BeO_2$	$K_2BeO_2 + K_3SbO_4 \leftarrow$ Beryllium antimonate
Magnesium chromite	$\rightarrow MgO + K_2CrO_4$	$K_2CrO_4 + K_3SbO_4 \leftarrow$ Chromium antimonate
Cadmium chromite	$\rightarrow CdO + K_2CrO_4$	$KAlO_2 + K_3SbO_4 \leftarrow$ Aluminium antimonate
Copper chromite	$\rightarrow CuO + K_2CrO_4$	$K_3SbO_4 + MgO \leftarrow$ Magnesium antimonate
Cobalt chromite	$\rightarrow CoO + K_2CrO_4$	$K_3SbO_4 + CdO \leftarrow$ Cadmium antimonate
Nickel chromite	$\rightarrow NiO + K_2CrO_4$	$K_3SbO_4 + MnO_2 \leftarrow$ Manganese antimonate
Manganese chromite	$\rightarrow MnO_2 + K_2CrO_4$	$K_3SbO_4 + CoO \leftarrow$ Cobalt antimonate
Zirconium chromite	$\rightarrow K_2ZrO_3 + K_2CrO_4$	$K_3SbO_4 + NiO \leftarrow$ Nickel antimonate
Cerium chromite	$\rightarrow CeO_2 + K_2CrO_4$	$K_3SbO_4 + CuO \leftarrow$ Copper antimonate
Uranium chromite	$\rightarrow K_2U_2O_7 + K_2CrO_4$	$K_3SbO_4 + CaCO_3 \leftarrow$ Calcium antimonate
		$K_3SbO_4 + SrCO_3 \leftarrow$ Strontium antimonate
Zinc aluminate	$\rightarrow KAlO_2 + K_2ZnO_2$	$K_3SbO_4 + BaCO_3 \leftarrow$ Barium antimonate
Copper aluminate	$\rightarrow CuO + KAlO_2$	$K_3SbO_4 + ThO_2 \leftarrow$ Thorium antimonate
Cobalt aluminate	$\rightarrow CoO + KAlO_2$	$K_3SbO_4 + K_2ZrO_3 \leftarrow$ Zirconium antimonate
Nickel aluminate	$\rightarrow NiO + KAlO_2$	$K_3SbO_4 + K_2U_2O_7 \leftarrow$ Uranium antimonate
Manganese aluminate	$\rightarrow MnO_2 + KAlO_2$	$K_3AsO_4 + K_2ZrO_3 \leftarrow$ Zirconium arsenate
Chromium tungstate	$\rightarrow K_2WO_4 + K_2CrO_4$	$(K_2TiO_3) + K_3AsO_4 + TiO_2 \leftarrow$ Titanium arsenate
Zirconium tungstate	$\rightarrow K_2ZrO_3 + K_2WO_4$	$K_2CrO_4 + K_3AsO_4 \leftarrow$ Chromium arsenate
Zinc tungstate	$\rightarrow K_2WO_4 + K_2ZnO_2$	$K_2SnO_3 + K_3AsO_4 \leftarrow$ Tin arsenate
Copper tungstate	$\rightarrow CuO + K_2WO_4$	$K_2CrO_4 + K_3VO_4 \leftarrow$ Chromium vanadate
Nickel tungstate	$\rightarrow NiO + K_2WO_4$	$K_3VO_4 + K_2ZrO_3 \leftarrow$ Zirconium vanadate
Cobalt tungstate	$\rightarrow CoO + K_2WO_4$	$KCl + K_2CrO_4 \leftarrow$ Chromium chloride
		$K_3PO_4 + K_2CrO_4 \leftarrow$ Chromium phosphate

^a $SrSO_4$ is completely decomposed by boiling with 10% sodium carbonate solution and will not be present here. Anhydrous $CrCl_3$ is only partially decomposed by boiling with 10% sodium carbonate solution and aqua regia and will therefore be present here.

TABLE II

Crush and digest the fused mass with 1 N K_2CO_3 solution at which point all the compounds enclosed within the lines will pass into solution. Filter.

Residue: MgO , NiO , MnO_2 , CoO , CuO , CdO , K_2ZrO_3 , TiO_2 , $K_2U_2O_7$, IrO_2 , $SrCO_3$, $BaCO_3$, $CaCO_3$, CeO_2 , ThO_2 , RhO_2 , zirconium tellurate and oxides of Sc, Y, La and rare earths.

Boil with conc. HCl and conc. HNO_3 mixed in the proportions of 5 : 1.

Evaporate nearly to dryness; add dil. HCl to the residue and filter.

Residue: CeO_2 , ThO_2 , RhO_2 and zirconium tellurate.

Fuse with $KHSO_4$ in a silica crucible to convert them into sulphates. Dissolve the fused mass in dil. HCl. Treat with 2 N Na_2S reagent in excess followed by conc. HCl and 10-15 g of CH_3COONH_4 (solid). Boil to precipitate the sulphides of Rh and Te as completely as possible. Filter.

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Precipitate: Sulphides of Rh and Te. Mix with the sulphides of arsenic group (Table II)⁵.

Filtrate: Chlorides of Zr, Ce and Th. Boil off H_2S completely and mix the solution with iron and rare earths group solution (Procedure V I)⁵.

Precipitate: $WO_3 \cdot H_2O$; $SiO_2 \cdot H_2O$ and Ta_2O_5 . Treat with NaOH solution and filter.

Ppt. Ta_2O_5 . Test for Ta as usual.

Test for W and Si as usual.

Filtrate: Na_2WO_4 and Na_2SiO_3 .

Precipitate: $WO_3 \cdot H_2O$;

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decomposed completely by boiling with concentrated sodium carbonate solution. The sulphate passes into the sodium carbonate filtrate, SrCO_3 dissolves in the acid treatment and thus the insoluble residue does not contain SrSO_4 . Another advantage is that a number of complex salts, like phosphotungstic acid, which dissolve in the standard acid treatment and complicate the analysis of this solution for basic radicals, pass completely into the sodium carbonate filtrate and are quite easily detected in this solution.

By this removal of many substances such as lead sulphate, ferrocyanides, ferricyanides, nitroprussides and the oxides of molybdenum and tungsten, it is possible to do away with Procedures I and II² which involve treatment with a saturated ammonium acetate solution and 4 *N* caustic soda solution respectively. The insoluble residue left after the acid treatment is treated only with NH_4OH solution for the removal of silver chloride and tungstic acid and then fused with $\text{KOH} + \text{K}_2\text{CO}_3 + \text{KNO}_3$. The treatment of the insoluble residue is thus greatly simplified and consists mainly of two operations; namely, fusion with (a) $\text{KOH} + \text{K}_2\text{CO}_3 + \text{KNO}_3$ and (b) HHSO_4 .

(2) The various solutions obtained in the treatment of the fused mass are combined with the different groups of the scheme for the basic radicals. Thus the whole of the solution obtained after the extraction of the fused mass (not dissolved in K_2CO_3 solution) with concentrated acids (Table II) is combined with the main solution for the detection of the basic radicals. In the treatment with the K_2CO_3 solution, at one stage the solution contains only the metals of the arsenic group; this is combined with the thio salts-forming group of the main solution. At another stage a solution is obtained which contains only the metals of the aluminium group; this is combined with the aluminium group of the main solution. The detection of the insoluble substances thus involves only a few extra procedures of a comparatively simple nature owing to the amalgamation with the schemes for cations and anions. The new scheme may be taken as final because it will easily provide for any new insoluble substances that may be discovered.

Note

In the Table showing the behaviour of the insoluble substances on fusion with $\text{KOH} + \text{K}_2\text{CO}_3 + \text{KNO}_3$ only reactions of the newly discovered insoluble substances have been shown. The reactions of the other insoluble substances have already been demonstrated in an earlier paper³. In studying the behaviour of the insoluble substances on fusion with $\text{KOH} + \text{K}_2\text{CO}_3 + \text{KNO}_3$ both tables should be studied together.

SUMMARY

A simplified scheme for the detection of all types of insoluble substances has been proposed. This scheme is based on the amalgamation of the procedures employed in the detection of insoluble substances with the schemes for the detection of cations and anions and thus very considerably simplifies the procedures ordinarily applied.

RÉSUMÉ

Une méthode simplifiée d'identification de tous les types de substances insolubles est proposée.

ZUSAMMENFASSUNG

Es wird ein vereinfachtes Verfahren zur Identifizierung unlöslicher Verbindungen aller Typen beschrieben.

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TIRON AS A SPECTROPHOTOMETRIC REAGENT FOR THE ESTIMATION OF OSMIUM

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During the studies¹ on the spectrophotometric estimation of copper with tiron, the latter was found to give a reddish violet colour with osmium(IV) in the presence of sodium acetate. On the basis of this colour reaction, a method reported herein, for the estimation of osmium(IV), has been derived.

The coloured complex, with maximum and minimum absorptions at 470 m μ and 410 m μ , respectively, obeys Beer's law; the optimum range with the minimum error lies between 8 and 24 p.p.m. of osmium. The sensitivity of the reaction is 0.2 p.p.m., i.e., 0.033 μ g per cm² according to the definition of SANDELL.

The sodium acetate, besides controlling the pH of the solution between 4.9 and 5.5 (the optimum region of complex formation), aids the colour development. For the full development of the colour, heating for a period of 15 min on a boiling water bath is essential. The colour so formed is stable for a period of 4 to 6 h. Longer periods slowly deepen the colour, and a higher pH shifts the maximum absorption region to a lower wavelength.

EXPERIMENTAL

Apparatus and solutions

Hilger's U.V. spectrophotometer was used for measuring the absorption of solutions in quartz absorption cells of 1-cm light path and with a tungsten filament lamp as the light source. Corrections, wherever necessary, were made to compensate for slight differences in the optical transmission of the cells.

pH measurements were made with a Cambridge pH indicator provided with an all-purpose (pH 1-13) glass electrode.

A weighed quantity of the chloro osmate (K_2OsCl_6) of JOHNSON AND MATTHEY was dissolved in 1N hydrochloric acid solution. The final concentration of osmium per ml of the solution was 0.2 mg.

A 5% solution of the reagent, tiron, disodium salt of 1,2-dihydroxybenzene 3,5-disulphonate, was prepared in the same way as reported in an earlier paper¹.

A 5N solution of sodium acetate was prepared and used for adjusting the pH of the colour solution.

For the study of the effect of diverse ions, solutions of the ions were prepared from their reagent-grade samples.

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Spectral transmittancy

An aliquot portion of the solution of osmium, mixed with 5 ml each of the tiron and the sodium acetate solutions added successively, was diluted with water to a volume of 20 ml and heated on the boiling water bath for 15 min. After cooling in ice water, the solution was transferred to a 25-ml volumetric flask where its volume was made up with water. A reagent blank with 1% tiron and 1% sodium acetate was also prepared in exactly the same way as previously stated. Spectral transmittancies for the solutions prepared were then measured. Curves A and B in Fig. 1 show the transmittancy of 8 p.p.m. of osmium against water and reagent blanks, respectively, and curve C exhibits the absorbancy of the reagent against the water blank. From the figure it is quite clear that the maximum absorption of the color system was at 410 μ , while the absorption is minimum at 410 μ .

Effect of time, temperature, pH and reagent

Full development of colour, even in the presence of sodium acetate, takes place only when the solution is heated for about 15 min. In about 3 min time the colour just appears and in 15 min the intensity is maximum. Further heating has no effect. After such development, the colour, which remains practically at a constant intensity at room temperature for about 4 to 5 h, is usually measured. Over longer periods of time, the colour slowly deepens.

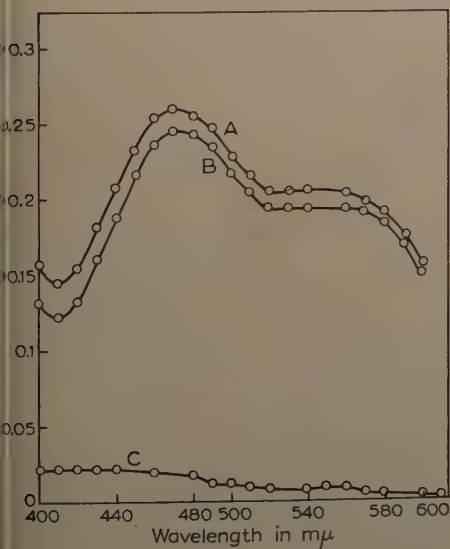


Fig. 1. Absorbance curves (A) 8 p.p.m. Os^{+4} against water blank; (B) 8 p.p.m. Os^{+4} against reagent blank; (C) Absorption of reagent against water blank.

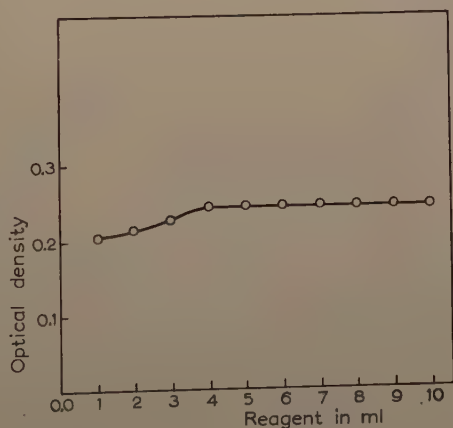


Fig. 2. Effect of reagent.

The nature and the maximum absorption region of the coloured complex being dependent on the pH, a thorough study of the effect of the latter justifies adjustment of the pH of the solution between 4.9 and 5.5, by sodium acetate. A pH higher than

5.5 decreases the intensity of the colour and changes the region of maximum absorption to a lower wavelength. The colour is not fully developed if the pH of the solution is maintained at a value lower than 4.9.

A study of the reagent concentration, on the colour system formed at pH 4.9 to 5.5, with different quantities (1 to 10 ml) of the reagent solution, added to 8 p.p.m. of osmium in solution in the manner described above, indicates (Fig. 2) that in a volume of 25 ml the amount of reagent required is only 4 ml. For all subsequent studies, 5 ml of the reagent were always used for a total volume of 25 ml.

Beer's law

For the study of the variation in O. D. with the concentration of osmium, solutions with different quantities of osmium(IV) were treated separately for their maximum colour development and their absorbancies were then measured at $470\text{ m}\mu$ against a reagent blank. The curve in Fig. 3, obtained by plotting the O. D. against the concentration of osmium, from 2 to 32 p.p.m., is a perfect straight line passing through the origin. The molar extinction coefficient as calculated from Beer's law is 5706.

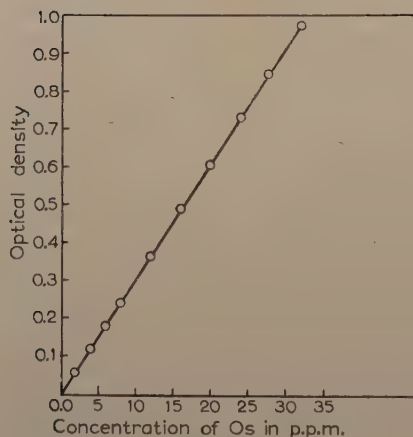


Fig. 3. Beer's law curve.

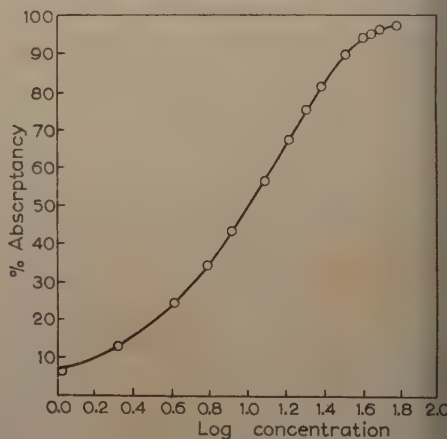


Fig. 4. Standard curve for osmium-tiron complex.

Optimum range

Though the colour system obeys Beer's law from 2 to 32 p.p.m. of osmium, the optimum concentration range as obtained from the steep portion of the curve (Fig. 4) formed by plotting % absorbancy as ordinate and log of concentration as abscissa, is 8 to 24 p.p.m. The relative analysis error per 1% absolute photometric error is 2.878%.

Effect of diverse ions

Fe^{+3} , Ti^{+4} , Nb^{+5} , Ta^{+5} , Ce^{+4} , UO_2^{+2} , CrO_4^{-2} , MoO_4^{-2} , OsO_4 and VO_3^- interfere by forming coloured complexes as do other platinum metals, except platinum itself. Ag^{+} and Au^{+3} are reduced to metal, while Pt is tolerated to the extent of 10 times the amount of osmium. Al^{+3} , Ca^{+2} , Ba^{+2} , Sr^{+2} , Sn^{+4} , Pb^{+2} , Zr^{+4} , Th^{+4} , Hg^{+2} and WO_4^{-2}

in the presence of sodium acetate. The regions of maximum and minimum absorptions are at $470\text{ m}\mu$ and $410\text{ m}\mu$, respectively, and the system obeys Beer's law from 2 to 32 p.p.m. of osmium. But the optimum range, with the relative analysis error of 2.878% per 1% absolute photometric error, is from 8 to 24 p.p.m. of osmium. The sensitivity of the reaction is $0.033\text{ }\mu\text{g/cm}^2$ (SANDELL) and the molar extinction coefficient is 5706. In solution, the complex is formed when the osmium and the reagent are in a ratio of 1:1; it has an instability constant equal to approximately $5.57 \cdot 10^{-5}$.

RÉSUMÉ

Le tiron est proposé comme réactif pour le dosage spectrophotométrique de l'osmium. Le complexe rouge violet obtenu est stable. Absorption maximum à $470\text{ m}\mu$; sensibilité $0.033\text{ }\mu\text{g/cm}^2$; coefficient d'extinction molaire 5706.

ZUSAMMENFASSUNG

Als Reagenz zur spektrophotometrischen Bestimmung von Osmium wird Tiron vorgeschlagen, das mit Osmium einen stabilen, rotviolett gefärbten Komplex bildet. Absorptionsmaximum bei $470\text{ m}\mu$; Empfindlichkeit: $0.033\text{ }\mu\text{g/cm}^2$; molarer Extinktionskoeffizient: 5706.

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THE DETECTION OF PRESERVATIVES IN WOOD WITH PYROCATECHOL VIOLET

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INTRODUCTION

The presence of preservatives in wood impregnated with water-soluble preservatives frequently cannot be detected visually because the salts are either colourless or masked by the natural colour of the wood. This masking effect is particularly so with the lower retentions used in the treatment of wood for use out of contact with the ground. In consequence, chemical spot tests have been developed to detect various preservative components in wood. FEIGL¹ has suggested tests for mercury, zinc, and copper salts as well as for sodium fluoride. The American Wood Preservers' Association² has proposed tests for copper, zinc and arsenic, while tests for the presence of boron have recently been reviewed by WILSON³.

The preservatives used in New Zealand are zinc-copper-chrome-arsenate, copper-chrome-arsenate, fluoride-chrome-arsenate-phenol, acid copper chromate with or without boric acid and boric acid-borax mixtures. In this laboratory the tests given in Table I have been used to detect and identify these preservatives.

With the exception of the test for boron, however, these procedures are of little value in field testing, for the reagents are either too sensitive, occasionally giving tests which are positive on untreated samples, or because the reagent solutions are not stable for more than a few days. Further, to identify any of the current preservatives

TABLE I

SPOT TESTS FOR THE IDENTIFICATION OF PRESERVATIVES IN WOOD

Reagent	Preservative					
	Zn-Cu-Cr-As	Cu-Cr-As	NaF-Cr-As-DNP	Cu-Cr	Cu-Cr-B ₂ O ₃	B ₂ O ₃
Dithizone in CHCl ₃	Violet red	Deep brown	—	Deep brown	Deep brown	—
% Diphenyl -bazide in acetone	Violet pink	Violet pink	—	Violet pink	Violet pink	—
polybdate ² benzidine SnCl ₂	Blue	Blue	Blue	—	—	—
mercuric ³ + acid	—	—	—	—	Red	Red

requires at least three separate reagents, of which two are two-solution types. For these reasons field testing is infrequently used, and in practice samples are submitted to the laboratory for examination.

SUK AND MALAT⁴ have described the properties of Pyrocatechol Violet (PCV). Since it gives colour reactions with many cations and some anions, notably borate, it seemed likely that this reagent might offer promise in the detection of preservatives. Its reaction is, however, given by arsenic.

TABLE II

THE REACTION OF PYROCATECHOL VIOLET WITH VARIOUS IONS IN WOOD

Ion	Retention as % ion in wood				
	0.55	0.28	0.15	0.07	0.04
As ³⁺	Brick-red	Red-brown	Brown-yellow	Green-yellow	Green-yellow
As ⁵⁺	Deep blue	Deep blue	Deep blue	Deep blue	Deep blue
As ⁶⁺	Deep blue	Deep blue	Deep blue	Blue green	Green-yellow
As ^{3a}	—	—	—	—	—
As ⁵⁺	Red-brown	Red-brown	Red-brown	Brown-yellow	Green-yellow

^a All samples gave a deep blue colour after some hours

TABLE III

THE REACTION OF PYROCATECHOL VIOLET WITH PRESERVATIVES IN WOOD

Preservative	Retention as % anhydrous salt				
	4.60	2.30	1.16	0.56	0.30
-Cu-Cr-As	Blue	Blue	Bluish-red	Red-brown	Red-brown
-Cr-As	Blue	Blue	Blue	Blue	Blue
F-Cr-As-DNP ^{a,b}	—	—	—	—	—

^a 2 : 4 Dinitrophenol

^b Blue colour develops after some hours in all cases

References p. 154

EXPERIMENTAL

Qualitative tests

It has been found that positive tests are obtained on *P. radiata* wood impregnated with Cu^{+2} , Cr^{+6} , Cr^{+3} , Zn^{+2} and BO_3^{-3} when the reagent is applied as a 0.1% aqueous solution buffered with ammonium acetate. These results are shown in Table II, while results obtained on *P. radiata* impregnated with preservatives are given in Table III.

These tests are also obtained on freshly treated wood. Untreated wood assumes a yellow colouration with the reagent. The boron test tends to intensify over some hours, but the transitional concentration between a definite positive test and a negative test lies in the region of 0.30 to 0.15% boric acid in the oven-dry wood and is obtained immediately, as with the turmeric test. The boron complex is masked by mannitol. Fluoride enhances the colour of the boron test. Zinc-copper-chrome-arsenate contains only a small proportion of copper, and this accounts for the change in colour at the higher concentrations. Other concentrations and acidities of the reagent were also tested but these offered no advantage over the 0.1% solution in ammonium acetate.

As the reaction with metal ions is masked by ethylenediaminetetraacetic acid (EDTA), the possibility of estimating preservative loadings by additions of EDTA to the reagent mixture was studied and the results given in Table IV show this is certainly the case with copper-chrome-arsenate treated wood. The other preservatives were not studied in this respect.

TABLE IV
THE EFFECT OF EDTA ON THE PCV REACTION WITH COPPER-CHROME-ARSENATE

Reagent	Retention as % anhydrous salt				
	4.60	2.30	1.16	0.56	0.30
0.1% PCV + buffer	Blue	Blue	Blue	Blue	Blue
0.1% PCV + buffer + 0.05% EDTA	Blue	Blue	Blue	Blue-yellow	Yellow
0.1% PCV + buffer + 0.1% EDTA	Blue	Blue	Blue-yellow	Yellow	Yellow

Detection of arsenate and fluoride

SUK AND MALAT⁴ state that molybdate, thorium and zirconium form blue complexes with Pyrocatechol Violet in acid solution. It has been found that this reaction is masked by arsenate, fluoride, and phosphate and only the red colour of the reagent in acid solution is obtained. Application of these facts to the detection of arsenate and fluoride in wood showed that an excellent indication of the presence of these anions is given with the zirconium compound, but the results were not absolutely unequivocal in the case of molybdate and thorium if copper was present, as, on standing, a gradual development of the blue copper complex tended to mask the reddish pink colour developed by the mixed reagent in the presence of the arsenate and fluoride. The zirconium complex forms in more acid solution (pH 1), and sufficient acid

TABLE V

THE REACTION OF PCV-ZIRCONIUM COMPLEX WITH ARSENATE-CONTAINING WOOD

Reagents	Retention as % As_2O_5 in wood				
	5.0	2.5	1.25	0.6	0.3
0.05% PCV 0.05% $ZrOCl_2$ pH 1	Red	Red	Red	Red	Red
0.05% PCV 0.1% $ZrOCl_2$ pH 1	Red	Red	Red	Red	Red
0.05% PCV 0.2% $ZrOCl_2$ pH 1	Red	Red	Red	Blue	Blue
0.05% PCV 1.0% $ZrOCl_2$ pH 1	Red	Red	Red-blue	Blue	Blue

present to prevent formation of the copper derivative. The colour change is from blue to reddish pink in the presence of arsenate or fluoride. Further experiments where an excess of zirconium was present indicated that some estimate of the amount of arsenate present could be obtained. These results are given in Table V. The fluoride reaction was not further studied, as fluoride containing preservatives are now not extensively used in this country.

CONCLUSIONS

From the foregoing results spot tests using pyrocatechol violet can now be proposed for the detection of preservatives, and the following test solutions are proposed and have been adopted in this laboratory:

Reagent I. 0.1% aqueous solution of Pyrocatechol Violet buffered with 5% ammonium acetate.

Reagent II. 0.05% solution of Pyrocatechol Violet in *N*/10 hydrochloric acid with 0.05% zirconium oxychloride added.

For field testing, where it is merely desired to determine whether the sample is treated with any of the above preservatives, Reagent I will in general be found to be all that is required. As the reagent is not very stable in alkaline solution, it is further recommended that the stock solution of the pyrocatechol violet be made in water and sufficient of the test solution be prepared for each day's testing by the addition of solid ammonium acetate to a portion of the stock solution. The mixed reagent should keep for several days, but the stock solution is stable for many weeks⁴. The information in Tables II and III will then allow any sample to be classed as treated or untreated.

Reagent II will allow the preservative to be classified as containing or not containing arsenic or fluoride, depending on whether the spot becomes pink or remains deep blue.

Where an estimate of the loading is required, this can easily be given using reagent

I with boron-treated wood or by using modified reagents I and II in the case of metal ion- or arsenic-containing wood respectively. No definite composition for these reagents is given, for the desired loading of preservative will vary with the end use of the timber. A series of experiments will, however, quickly give the most satisfactory solution to use for any particular retention of preservative.

In practice, the preservatives listed above, with the exception of boric acid-borax, are usually applied by pressure processes, and salt gradients are not as important as an estimate of completeness of sapwood penetration. Therefore, a clear delineation of the untreated area will satisfy most requirements for testing. This is obtained with either reagent I or II and the modified reagents could well be restricted to laboratory examinations.

The results given above deal with tests carried out using the slightly coloured *P. radiata* wood. The tests have, however, been also applied to the highly coloured indigenous timbers such as rimu, *Dacrydium cupressinum*, and have been found to give good results although blank tests assume the natural colour of the wood. The boron test is especially satisfactory on such timbers as the neutral character of the reagent does not cause the development of the purple colours given by the acid used in the turmeric test and which in many cases effectively masks the test.

ACKNOWLEDGEMENT

The writer is indebted to Mr. A. J. McQUIRE for the preparation of the test pieces used in this study, to the Director of Forestry for permission to publish.

SUMMARY

The detection of As^{+5} , BO_3^{-3} , Cu^{+2} , Cr^{+3} , Cr^{+6} , Zn^{+2} , and F^- in treated wood with Pyrocatechol Violet is described.

RÉSUMÉ

L'auteur décrit une méthode utilisant le violet de pyrocatechol pour l'identification de As^{+5} , BO_3^{-3} , Cu^{+2} , Cr^{+3} , Cr^{+6} , Zn^{+2} , F^- dans des bois traités.

ZUSAMMENFASSUNG

Es wird eine Method vorgeschlagen zum Nachweis von As^{+5} , BO_3^{-3} , Cu^{+2} , Cr^{+3} , Cr^{+6} , Zn^{+2} , and F^- in imprägniertem Holz unter Verwendung von Pyrocatechol Violet.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES
WITH A ROTATED ALUMINUM WIRE ELECTRODETHE R.A.L.E. AS INDICATOR ELECTRODE IN POTENTIOMETRIC AND
AMPEROMETRIC ACID-BASE TITRATIONS

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In the first paper of this series¹ it was shown that the rotated aluminum electrode (R.A.L.E.) does not function as a pH electrode in acid medium but behaves as a pOH electrode at a pH greater than about 9. Even traces of fluoride ion depolarize the electrode in acid solutions and the electrode potential then becomes considerably more negative than in the absence of fluoride. In order to know the limitations of the R.A.L.E. as indicator electrode in potentiometric acid-base titrations in aqueous medium, both in the absence and presence of fluoride in the solution, potential measurements have been made in acid buffer solutions containing varying concentrations of fluoride. Moreover voltammograms were run and measurements of the stationary potential (zero-current potential) of the electrode were made in buffer solutions of various composition in the pH range between 6 and 11, both in the presence and absence of fluoride.

No amperometric titrations of acids with a strong base have been described in the literature. Since hydroxyl ions yield anodic waves at the R.A.L.E.¹ with diffusion currents proportional to the concentration of hydroxyl ions, the amperometric titration of strong and intermediate weak acids with standard sodium hydroxide has been studied and the results are reported in the present paper. The end-point could be detected with accuracy and precision even at very low hydroxyl-ion concentrations. The method is very rapid and gives good results even at high dilutions. Examples are given in which the end-point can be detected with much greater accuracy than by classical methods. The limitations of the amperometric titration method are briefly stated.

The experimental technique was the same as that described in the previous paper¹. Unless otherwise stated, the experiments were carried out in the absence of oxygen.

EXPERIMENTAL RESULTS AND DISCUSSION

Potential measurements and voltammograms in absence of oxygen

Before each measurement the electrode was pretreated in EDTA buffer solution as described previously¹. The stationary potentials reported in Table I (absence of oxygen) were considered constant when the potential remained unchanged after waiting for another 5 min. The pH of the solutions was determined with the glass electrode after the potential of the R.A.L.E. had become constant. The time when this measure-

ment was made had an effect on the pH only in solutions composed mainly of bicarbonate; since nitrogen was swept through or over the solutions, some loss of carbon dioxide occurred continuously.

Although the potential of the R.A.E. in acid medium is poorly reproducible, the great effect of fluoride on the potential in acid media is clearly recognized in Table I.

TABLE I
EFFECT OF FLUORIDE ON THE POTENTIAL OF THE R.A.E. IN ACID AND ALKALINE BUFFERS

<i>Electrolyte</i>	<i>pH</i>	<i>NaF concentration M</i>	<i>-E vs. S.C.E.</i>
0.1 M HClO ₄	1.10	2 · 10 ⁻⁵	1.231
	1.10	1 · 10 ⁻⁴	1.297
	1.15	1 · 10 ⁻³	1.395
0.01 M HClO ₄	2.10	0	0.6 to 0.8 ^a
	2.10	2 · 10 ⁻⁵	1.242
	2.10	1 · 10 ⁻⁴	1.327
	2.15	1 · 10 ⁻³	1.432
0.1 M HAc + 0.01 M NaClO ₄	2.90	2 · 10 ⁻⁵	1.251
	2.95	1 · 10 ⁻⁴	1.357
	2.95	1 · 10 ⁻³	1.456
0.09 M HAc + 0.01 M NaAc	3.80	2 · 10 ⁻⁵	1.269
	3.80	1 · 10 ⁻⁴	1.391
	3.80	1 · 10 ⁻³	1.490
0.05 M HAC + 0.05 M NaAc	4.60	0	0.7 to 0.9 ^a
	4.60	2 · 10 ⁻⁵	1.273
	4.60	1 · 10 ⁻⁴	1.412
	4.65	1 · 10 ⁻³	1.505
0.01 M HAC + 0.09 M NaAc	5.60	0	0.7 to 0.95 ^a
	5.60	2 · 10 ⁻⁵	1.279
	5.60	1 · 10 ⁻⁴	1.427
	5.62	1 · 10 ⁻³	1.531
0.025 M KH ₂ PO ₄ + 0.0028 N NaOH	6.00	0	1.0 ^a
	6.00	2 · 10 ⁻⁵	1.0 ^a
	6.00	1 · 10 ⁻⁴	1.0 ^a
	6.00	1 · 10 ⁻³	1.3 ^a
0.025 M KH ₂ PO ₄ + 0.014 N NaOH	7.00	2 · 10 ⁻⁵	1.05 ^a
	7.00	1 · 10 ⁻⁴	1.05 ^a
	7.00	1 · 10 ⁻³	1.07 ^a
0.025 M KH ₂ PO ₄ + 0.0235 N NaOH	8.00	2 · 10 ⁻⁵	1.06 ^a
	8.00	1 · 10 ⁻⁴	1.06 ^a
	8.00	1 · 10 ⁻³	1.08 ^a
0.028 M Veronal + 0.05 M NaAc + 0.027 N HCl	6.30	0	1.0 ^a
	6.30	2 · 10 ⁻⁵	1.0 ^a
	6.30	1 · 10 ⁻⁴	1.1 ^a
	6.30	1 · 10 ⁻³	1.537
0.053 M Veronal + 0.046 N HCl	7.00	0	1.16 ^a
	7.00	2 · 10 ⁻⁵	1.17 ^a
	7.00	1 · 10 ⁻⁴	1.18 ^a
	7.00	1 · 10 ⁻³	1.429

TABLE I (continued)

Electrolyte	pH	NaF concentration M	-E vs. S.C.E.
0.071 M Veronal + 0.028 N HCl	8.05 8.05 8.05 8.05	0 $2 \cdot 10^{-5}$ $1 \cdot 10^{-4}$ $1 \cdot 10^{-3}$	1.522 1.525 1.527 1.536
0.005 M Na ₂ CO ₃ + 0.090 M NaHCO ₃	8.80 8.80 8.90	$2 \cdot 10^{-5}$ $1 \cdot 10^{-4}$ $1 \cdot 10^{-3}$	1.578 1.584 1.589
0.05 M Borax	9.25 9.25 9.25	$2 \cdot 10^{-5}$ $1 \cdot 10^{-4}$ $1 \cdot 10^{-3}$	1.59 1.59 1.60
0.05 M Na ₂ CO ₃ + 0.05 M NaHCO ₃	9.85 9.85 9.90	$2 \cdot 10^{-5}$ $1 \cdot 10^{-4}$ $1 \cdot 10^{-3}$	1.687 1.690 1.694
0.016 M Na ₂ CO ₃ 0.004 M NaHCO ₃	10.50 10.50 10.55	$2 \cdot 10^{-5}$ $1 \cdot 10^{-4}$ $1 \cdot 10^{-3}$	1.765 1.766 1.769
0.001 M Borax + 0.048 M Na ₂ CO ₃	10.90 10.95 10.95	$2 \cdot 10^{-5}$ $1 \cdot 10^{-4}$ $1 \cdot 10^{-3}$	1.775 1.775 1.777
0.01 N NaOH	12.2 12.2 12.2 (not measured)	0 $2 \cdot 10^{-5}$ $1 \cdot 10^{-3}$	1.851 1.850 1.855

* Potential ill defined; electrode highly polarized.

In alkaline medium ($\text{pH} > 8$) fluoride has no longer an effect on the potential, which is now determined solely by the hydroxyl ion concentration. It is particularly interesting to note that fluoride in phosphate buffers with pH between 6 and 8 does not affect the potential, which is extremely ill-defined. As a matter of fact, in these phosphate buffers fluoride does not depolarize the electrode and does not yield anodic wave. Some voltammograms in phosphate buffers are shown in Fig. 1. The current-potential curves are practically identical in the pH range between 6 and 9 and they remain unchanged in the presence of fluoride in concentrations as high as 10^{-3} M. On the other hand, hydroxyl ions depolarize the electrode in phosphate containing solutions with a pH greater than about 10. Typical examples of this depolarization at pH 10, 10.5 and 11 are illustrated by curves C, D and E in Fig. 1. It should be mentioned that after determining the equilibrium potential in phosphate buffer (pH 6 to 8) the electrode remained polarized in acid buffers containing fluoride. Apparently a film was formed which was not removed by EDTA. Anodic polarization in acid medium in the presence of 10^{-3} M fluoride restored the original properties of the electrode.

The observations described for phosphate buffer in the pH range between 6 and 8 do not seem to be specific for phosphate. Similar, but not identical observations have

been made in veronal buffers with a pH between 6 and 8. The R.A.E. remains strongly polarized even when the concentration of fluoride is equal to $1 \cdot 10^{-4} M$. However, in the presence of $10^{-3} M$ fluoride a pronounced anodic depolarization occurs. An example of this effect is given in Fig. 2.

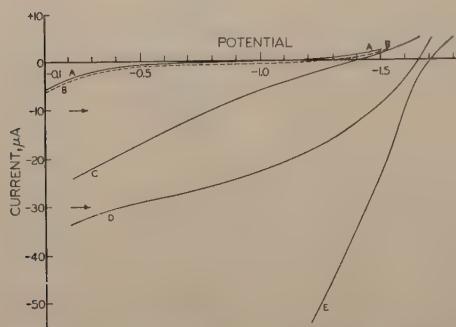


Fig. 1. Voltammograms in phosphate buffers. A, $0.05 M KH_2PO_4 + 0.047 N NaOH$, pH 8.1; B, $0.017 M KH_2PO_4 + 0.041 M borax$, pH 9.0; C, $0.01 M Na_2HPO_4 + 0.0004 N NaOH$, pH 9.9; D, $0.01 M Na_2HPO_4 + 0.0012 N NaOH$, pH 10.5; E, $0.05 M Na_2HPO_4 + 0.008 N NaOH$, pH 11.0.

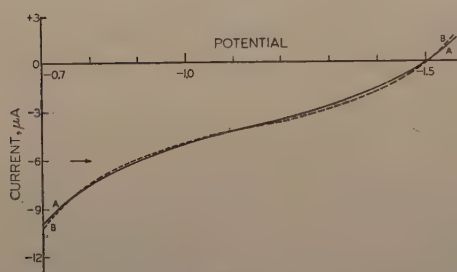


Fig. 3. Voltammograms in $0.071 M$ veronal + $0.028 N HCl$, pH 8.05. A, no addition; B, with $1 \cdot 10^{-3} M NaF$.

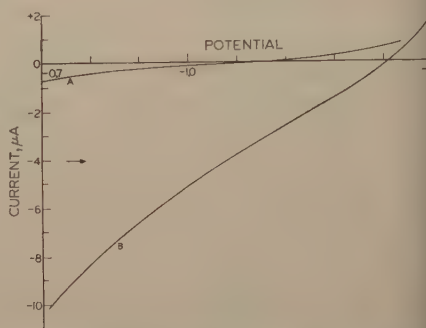


Fig. 2. Voltammograms in $0.053 M$ veronal + $0.046 N HCl$, pH 7.0. A, $1 \cdot 10^{-4} M NaF$; B, $1 \cdot 10^{-3} M NaF$.

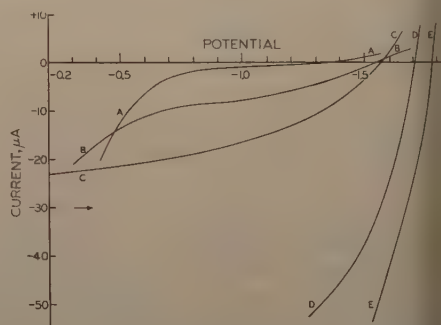


Fig. 4. Voltammograms in bicarbonate-carbonate buffers. A, $0.01 M$ sodium bicarbonate adjusted with HCl to pH 7.9; B, as A, pH 8.7; C, no addition, pH 9.0; D, adjusted with $NaOH$ to pH 10.0; E, as D, pH 11.0.

It is interesting to note that hydroxyl ions depolarize the electrode in a veronal buffer of pH 8. As can be seen from Fig. 3, fluoride in a concentration of $10^{-3} M$ in this buffer has no effect on the voltammogram.

Quite generally, the shapes of voltammograms and also the stationary potentials in the pH range between 8 and 10 vary somewhat with the kind and concentration of the buffer. As an example, some voltammograms in sodium carbonate-bicarbonate buffers are reproduced in Fig. 4. These curves are similar to but not identical with those observed in borate, ammonia-ammonium chloride and veronal buffers of the same pH.

The plot of potential *versus* pH in the presence of various concentrations of fluoride is shown in Fig. 5 has a very unusual shape. Between pH 1 and 5.5 the potential becomes 10 mV more negative per unit increase in pH at fluoride concentrations between 10^{-3} and 10^{-4} M. This value is only 10 mV at a fluoride concentration of $2 \cdot 10^{-5}$ M. The potential is extremely badly defined between pH 6 and 8. A continuous line (curve 3 in Fig. 5) is found only in veronal buffers in the presence of 10^{-3} M fluoride. In all

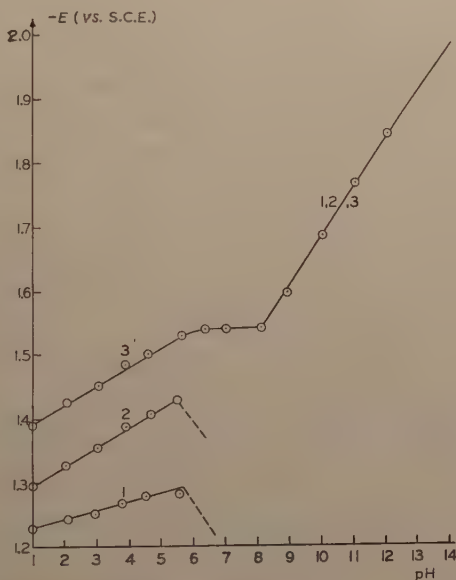


Fig. 5. Potential *versus* pH at various fluoride concentrations. 1, $2 \cdot 10^{-5}$ M NaF; 2, $1 \cdot 10^{-4}$ M NaF; 3, $1 \cdot 10^{-3}$ M NaF.

In other instances the potentials are highly irreproducible in the pH range between 6 and 8. In phosphate containing solutions the irreproducibility may be observed already at a pH of 5. In such solutions the potential is considerably less negative than may be expected from the curves in Fig. 5. For example, the electrode is strongly polarized in a 0.01 M monopotassium dihydrogen phosphate solution of pH 4.95 even in the presence of 10^{-4} M fluoride. A fluoride concentration of 10^{-3} M is necessary to bring about depolarization and a reproducible potential. This behavior accounts for the unusual titration lines in the titration of a mixture of a strong acid and monopotassium dihydrogen phosphate with a strong base (Fig. 8). At a pH greater than 8 the effect of fluoride on the potential is negligible and a straight line with a slope in the vicinity of 70 mV per unit change in pH is found. The values are in reasonable agreement with those reported previously¹. In acid medium and at constant pH the electrode potential becomes 100 ± 2 mV more negative when the fluoride concentration is increased from 10^{-4} to 10^{-3} M. The depolarization of the aluminum electrode by fluoride may be expected to be given by:



or



If these reactions were reversible and if the concentration and also the composition of $\text{AlF}_n^{(3-n)+}$ were constant (slightly soluble), the following expression for the potential at a given pH can be derived:

$$E = \text{Constant} + \frac{RT}{3F} \ln \frac{1}{\Sigma[\text{F}^-]} \quad \dots \dots \dots (3)$$

in which $\Sigma[\text{F}^-]$ is the total concentration of fluoride ($[\text{HF}] + [\text{F}^-]$). Under these conditions n then would be equal to 5 at fluoride concentrations between 10^{-4} and $10^{-3} M$. It seems doubtful whether the above assumptions are justified and no further application of equations (1) or (2) is proposed until measurements have been made in solutions in which $[\text{AlF}_n^{(3-n)+}]$ is better defined.

Sensitivity of electrode for traces of fluoride

It has been stated that the potential of the R.A.I.E. in acid medium is poorly reproducible. The electrode is highly polarized and potentials vary from day to day probably because of incomplete reproducibility of the surface. Since the potential in acid medium in the absence of fluoride is so poorly reproducible, it is impossible to give an exact figure of the effect of a trace of fluoride upon the potential. However, the data in Table II illustrate that the R.A.I.E. is a very sensitive indicator electrode for the detection of fluoride. In an acetate buffer we have always found the potential to be less negative than -1.0 V (*vs.* S.C.E.) in the absence of fluoride. It is fair to

TABLE II
SENSITIVITY OF THE POTENTIOMETRIC DETECTION OF FLUORIDE

Medium	pH	Fluoride concentration Molar	$-E$ <i>vs.</i> S.C.E.	Time to attain stationary potential min
0.1 M HClO_4	1.1	0	0.8(0.6–0.8)	~60
	1.1	$1 \cdot 10^{-6}$	0.85	35
	1.1	$1 \cdot 10^{-5}$	1.17	35
	1.1	$2 \cdot 10^{-5}$	1.23	15
0.09 M HAc + 0.01 M NaAc	3.8	0	0.8–1.0	~60
	3.8	$1 \cdot 10^{-6}$	1.06	40
	3.8	$1 \cdot 10^{-5}$	1.20	25
	3.8	$2 \cdot 10^{-5}$	1.27	15
		$2 \cdot 10^{-5}$	1.26 ^a	
		$2 \cdot 10^{-5}$	1.24 ^b	

^a In presence of 0.01 M Na_2SO_4

^b In presence of 0.01 M KH_2PO_4

state that a potential of -1.05 V in an acetate buffer of pH 3 to 4 definitely indicates the presence of fluoride in the solution. The sensitivity of this test is of the order of $5 \cdot 10^{-6} M$ fluoride, corresponding to about 0.1 p.p.m. of fluoride. Since the potential in the fluoride-free acetate buffer depends on the previous history of the electrode, it is recommended that this potential be determined first before measuring the poten-

of the unknown. The test is highly selective and is not interfered with by moderate concentrations of sulfate, phosphate and other common ions. We have applied the test to the detection of fluoride in six different potable water species and were able to detect 0.2 p.p.m. of fluoride with certainty. The test must be carried out in the absence of oxygen. Other oxidizing agents (copper, silver ions, permanganate) make the electrode potential less negative and must be removed.

Effect of oxygen on the fluoride potential and on the anodic waves at the R.Al.E. in acid media

In the first paper of this series it was stated that oxygen does not affect the poorly reproducible potential of the R.Al.E. in acid medium. There is no indication of cathodic depolarization of the electrode by oxygen. However, the situation is entirely different in the presence of fluoride. Voltammograms and potentials were determined in 0.1 and 0.01 *M* perchloric acid and in acetate buffers with a pH varying between 2 and 4.6, all solutions being 10^{-4} *M* in fluoride and either saturated with oxygen or made oxygen-free with the aid of pure nitrogen. After the stationary potential in the nitrogen saturated solution had been established, a current-potential curve was run from positive to negative potentials. The solution was then saturated with oxygen and the procedure repeated. Qualitatively, the effect of oxygen was the same in all solutions; oxygen shifts the anodic wave and the potential to less negative values (Table III), and in some instances the diffusion current of fluoride is not attained in the oxygen saturated solutions. An illustration of this effect is given in Fig. 6; some quantitative data on the magnitude of the shift of the "fluoride potential" by oxygen are reported on Table III. The effect of oxygen on the potential is considerably smaller at a pH of 1 than it is in less acid solutions (pH 3.8 and 4.6). The presence of fluoride in the solution appears to facilitate the reduction of oxygen at the R.Al.E.

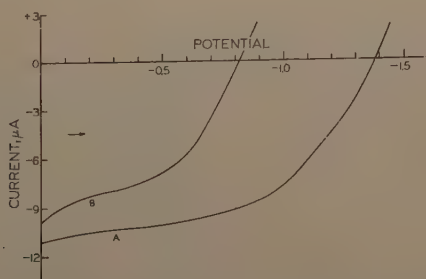


Fig. 6. Voltammograms of fluoride in presence and absence of oxygen; $1 \cdot 10^{-4}$ *M* NaF in 0.09 *M* HAc + 0.01 *M* NaAc, pH 3.8. A, saturated with nitrogen; B, saturated with oxygen.

TABLE III

EFFECT OF OXYGEN ON THE POTENTIAL (E) OF THE R.Al.E. IN 10^{-4} *M* FLUORIDE SOLUTION

Electrolyte	pH	$-E_{Na}$ vs. S.C.E.	$-E_{O_2}$ vs. S.C.E.	ΔE V
0.1 <i>M</i> HClO ₄	1.1	1.295	1.081	0.214
0.09 <i>M</i> HAc + 0.01 <i>M</i> NaAc	3.8	1.387	0.822	0.565
0.05 <i>M</i> HAc + 0.05 <i>M</i> NaAc	4.6	1.405	0.891	0.514

The potentials measured in the presence of oxygen are therefore typical "mixed potentials"². At such a potential the anodic fluoride current is equal to the cathodic oxygen current. For example, in Fig. 6 the fluoride current in a nitrogen atmosphere at a potential of -0.82 V is approximately $9 \mu\text{A}$, but in an oxygen-saturated solution it is apparently equal to zero. Actually, in the latter solution the anodic fluoride current would be expected to be $9 \mu\text{A}$ while it is compensated by an oxygen reduction current of equal magnitude. Other examples of mixed potentials at an aluminum electrode in ceric sulfate in acid medium and in ferricyanide in acid and alkaline media have been reported by PETROCELLI^{3,4}.

Potentiometric acid-base titrations

In the preceding sections and the previous paper¹ it has been stated that the potential of the R.A.L.E. is not well defined in acid medium and that the electrode does not function as a pH electrode until the hydroxyl-ion concentration is about $10^{-6} M$ or greater. During a potentiometric titration of an acid with a strong base the potential was found to vary very little in the pH range between 1 and 8, but it becomes very much more negative when the pH increases further. Use of this fact has been made by SCARANO⁵ who has described acid-base titrations using aluminum as an indicator electrode.

Curve A in Fig. 7 represents the titration curve of 50 ml of $0.01 N$ hydrochloric acid with $0.127 N$ standard carbonate-free sodium hydroxide. In the immediate vicinity of the end-point, a large break in potential from about -0.95 to -1.6 V is observed. The potentiometric end-point (first and second derivatives) could be determined with an accuracy and precision of 0.2% . As could be expected, the break in potential becomes considerably less pronounced in the presence of a trace of fluoride (see Table I and curve B in Fig. 7). Practical advantages of adding a trace of fluoride to the so-

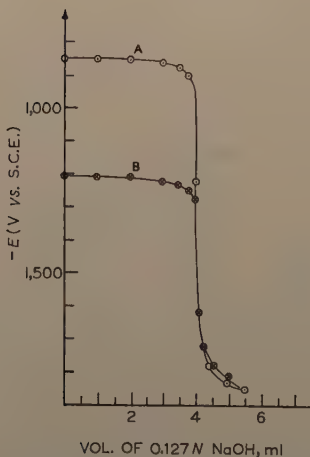


Fig. 7. Titration curves of $0.01 N$ HCl with $0.127 N$ NaOH. A, absence of fluoride; B, $2 \cdot 10^{-5} M$ NaF added. Calculated stoichiometric end-point 3.997 ml; found: 3.990 ml.

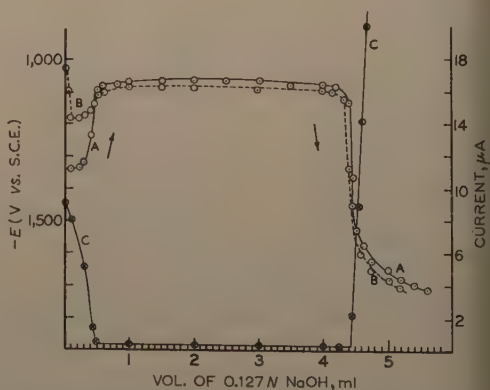


Fig. 8. Potentiometric and amperometric titration curves of a mixture of $0.001 N$ HCl + $0.01 M$ KH_2PO_4 , in the presence and absence of $1 \cdot 10^{-4} M$ NaF. Applied potential in the amperometric titration: -1.0 V (vs. S.C.E.). A, potentiometric curve in the presence of $1 \cdot 10^{-4} M$ NaF; B, same as A, in the absence of fluoride (dotted line); C, amperometric curve in presence of $1 \cdot 10^{-4} M$ NaF.

ion to be titrated, are that the potential becomes well defined in acid medium and that it takes much less time to attain its constant value at a pH smaller than 8. When 0.001 *N* hydrochloric acid could be titrated (absence of fluoride) with an accuracy and precision of 2%. Similarly, 0.001 *N* solutions of acetic acid and of potassium biphthalate were titrated with the same accuracy in the absence or presence of fluoride. In the absence of fluoride these titrations are much less time consuming if standard base is added until an "end-point potential" of -1.20 V is attained. This potential corresponds to an end-point pH of about 8. A very interesting plot (Fig. 8) is observed in the titration of a mixture of a strong acid and monopotassium dihydrogen phosphate containing a trace of fluoride, with sodium hydroxide. In such a mixture two potential breaks are obtained (curve A in Fig. 8). The first end-point, corresponding to the neutralization of the strong acid, is indicated by a potential peak in the "wrong" direction (from negative to more positive potentials). The potential hardly changes during the neutralization of the free strong acid in the absence of fluoride. Immediately after neutralization of the strong acid the electrode becomes highly polarized, even though fluoride is present (see Table I) and the potential becomes some 250 mV less negative. The potential then hardly changes during the neutralization of dihydrogen phosphate to monohydrogen phosphate until very close to the end-point (pH around 8) when the electrode becomes depolarized by hydroxyl ions. A large break in potential of the order of 500 mV is observed at the end-point. The first end-point was found after addition of 0.41 ml 0.127 *N* standard base (calculated 0.40 ml) and the second end-point after addition of 4.43 ml (calculated 4.0 ml). It is evident from Fig. 8 that in the absence of fluoride the first end-point is made less pronounced by the polarization of the electrode by the phosphate. The second end-point corresponding to monohydrogen phosphate is found at the right position either in the absence or presence of fluoride, which substantiates the conclusion that fluoride in alkaline medium has practically no effect upon the potential. It is hardly to be expected that the R.Al.E. will find much application in acid-base titrations in aqueous media, since the glass electrode and other pH indicating electrodes respond much more quickly and yield much more reliable data of the pH during a titration. For this reason, the limitations of the R.Al.E. in potentiometric acid-base titrations will not be discussed. It is possible, however, that the electrode may find wider application in non-aqueous titrations. It is planned to study the use of the electrode under such conditions.

Amperometric acid-base titrations

As has been shown in the first paper of this series¹ hydroxyl ions depolarize the aluminum electrode yielding an anodic wave with a well defined diffusion current at -1.0 V vs. S.C.E. Thus, it may be expected that strong and weak acids with a dissociation constant greater than about 10^{-6} can be titrated amperometrically with strong base. The titration can be carried out very rapidly, even in very dilute solutions. For example, the amperometric titration of 0.001 *N* hydrochloric acid with 0.1 *N* carbonate-free standard sodium hydroxide at -1.0 V (S.C.E.) gave results which were accurate and precise to within 2%. Similar results were obtained in the titration of 0.001 *N* acetic acid and biphthalate. As an illustration, the amperometric titration curve of 0.001 *M* potassium biphthalate is given in Fig. 9. The right hand ordinate gives the values of the diffusion current of free hydroxyl ions after

the end-point. For comparison the potentiometric titration curve is also plotted. In the amperometric titration of $0.00025\text{ }N$ biphthalate the end-point was found with an accuracy of 5%.

The titration of a mixture of $0.001\text{ }N$ hydrochloric acid and $0.01\text{ }M$ monopotassium phosphate in the presence of $10^{-4}\text{ }M$ fluoride can also be followed amperometrically,

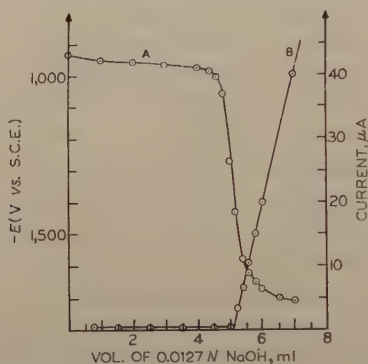


Fig. 9. Potentiometric and amperometric titration curves of $0.00127\text{ }M$ potassium biphthalate; applied potential in the amperometric titration: $-1.0\text{ V (vs. S.C.E.)}$. A, potentiometric curve, end-point, 4.95 ml; B, amperometric curve, end-point, 5.05. Calculated end-point: 5.00 ml.

and the titration lines are shown in Fig. 8. In the presence of free acid an anodic fluoride current is measured at -0.1 V . This current is less than the diffusion current since the phosphate starts to interfere at a pH around 4. At a pH of about 5.5 the electrode becomes completely polarized by the phosphate and the anodic current becomes zero. The titration line (curve C in Fig. 8) is not straight but curved. The extrapolated end-point gives about 20% high value for the neutralization of the strong acid.

After complete neutralization of the dihydrogen phosphate to monohydrogen-phosphate an anodic current is measured again. This current is caused by hydroxyl ions and it increases with excess of base (curve C in Fig. 8). The second end-point was found after addition of 4.41 ml of standard base (calculated 4.40 ml).

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SUMMARY

The effect of varying concentrations of fluoride on the potential of the R.A.I.E. in acid buffer solutions is reported. In the pH range between 1 and 5.5 the potential becomes 30 mV more negative per unit increase in pH at fluoride concentrations between 10^{-3} and $10^{-4}\text{ }M$. At a given pH the potential becomes 100 mV more negative when the fluoride concentration is increased from 10^{-4} to $10^{-3}\text{ }M$. No depolarization occurs and no reproducible potentials can be measured in phosphate buffers of pH 6 to 8, even in the presence of $10^{-3}\text{ }M$ fluoride. This concentration of fluoride causes depolarization and establishment of reproducible potentials in veronal buffers of reproducible pH 6 to 8. At a pH greater than 9 fluoride has no effect on the electrode potential which now becomes determined by pH. In the presence of fluoride, oxygen shifts the electrode potential to less negative values (mixed potential). Examples of potentiometric and amperometric titrations of strong and weak acids are given with the R.A.I.E. as indicator electrode.

RÉSUMÉ

Les auteurs ont étudié l'influence de concentrations variables de fluorure sur le potentiel d'une électrode tournante d'aluminium, dans des solutions tampon acides à divers pH. Des exemples de titrages potentiométriques et ampérométriques au moyen de l'électrode tournante d'aluminium sont donnés pour des acides forts et des acides faibles.

ZUSAMMENFASSUNG

Es wurde der Einfluss wechselnder Fluorid Konzentrationen auf das Potential einer rotierenden Aluminiumelektrode in sauren Pufferlösungen bei verschiedenem pH untersucht. Beispiele für potentiometrische und ampérometrische Titrationen starker und schwacher Säuren mit Hilfe der rotierenden Aluminiumelektrode werden angeführt.

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DETERMINATION OF MAGNESIUM IN NODULAR CAST IRON, USING A CHROMATOGRAPHIC SEPARATION

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INTRODUCTION

Trends in recent chemical methods for the determination of magnesium in cast iron have been towards simplified separation techniques, enabling results to be obtained quickly. This is shown by a comparison of the methods of GREEN¹, ZINDEL² and REICHERT³ with those of WESTWOOD AND PRESSER⁴, YARNE AND SOBERS⁵ and the A.S.T.M.⁶ SHIOKAWA AND SATO⁷ have successfully used an ion-exchange resin for the separation of small amounts of boron and magnesium from large quantities of iron. Apart from this work, chromatographic methods, which are simple and require little manipulation, do not appear to have received much attention. This prompted the author to investigate the possibilities of cellulose column chromatography, which has been used in the determination of other constituents of iron and steel⁸⁻¹⁰. A procedure taking about 4 h was developed, utilizing a volumetric finish with EDTA after the initial separation from interfering elements.

EXPERIMENTAL

Reagents

Solvent: Methyl ethyl ketone, reagent grade.
 Elution mixture: Methyl ethyl ketone 98 ml } freshly prepared.
 10 N Hydrochloric acid 2 ml }

* This work was undertaken in part fulfilment of the requirements for an Honours B.Sc. degree at the N.S.W. University of Technology, Sydney (Australia).

EDTA: Disodium salt (reagent grade) 3.7 g/l.

Indicator: 1% Eriochrome Black in equal parts of ethanol and triethanolamine.

Buffer solution: Ammonium chloride 6.75 g } per 100 ml
 15 N Ammonia 57 ml }

Ascorbic acid: Reagent grade.

Preliminary experiments

The elution mixture was chosen on the basis of tests with a synthetic cation mixture, chromatographed on paper strips (ascending solvent). Iron was readily separated from magnesium and manganese which remained at R_F 0-0.1. Further tests with cellulose columns indicated that magnesium was retained in the column until all iron and manganese had been eluted.

Column preparation

A uniform column about 9 cm long in a silicone-treated glass tube, 1.3 cm in diameter, was prepared from a slurry of Whatman's standard grade cellulose for chromatographic purposes. (5 g in 50 ml of N hydrochloric acid). The column was conditioned by washing successively with 50 ml of N hydrochloric acid, 150 ml of distilled water, 50 ml of solvent and 100 ml of elution mixture.

Procedure

1 g of iron was dissolved in 30 ml of 5 N hydrochloric acid; the hot solution was oxidised with 5 ml of 15 N nitric acid, then evaporated to dryness and baked for 5 min at about 200°. The residue was warmed with 15 ml of 10 N hydrochloric acid until the salts were dissolved; 25 ml of distilled water was added and the solution was heated to near boiling, then filtered. The residue was washed with hydrochloric acid and hot water, and the filtrate was evaporated just dry; the salts were re-dissolved in 4 ml of 10 N hydrochloric acid, with gentle warming. To the cooled solution, 10 ml of elution mixture was added; the mixture was swirled thoroughly, then poured onto the column. The beaker was rinsed with 2-ml portions of elution mixture. Two phases resulted, the lower layer being light yellow-brown in colour. Gentle suction was applied till the liquid level was just above the top of the column. The tube walls were washed with small portions of elution mixture, draining (without letting the top of the column become dry) between rinses. Finally, the tube was filled with elution mixture, and elution was continued at 1-2 ml/min until a total of 100 ml had passed through the column; the eluate was discarded. 80 ml of 1% hydrochloric acid was then passed through the column to recover the remaining metals. To this extract, 1 g of ammonium chloride was added, and the solution was made ammoniacal with 2 ml of 5 N ammonia in excess; the solution was heated to boiling, then 2 ml of 10% ammonium oxalate was added dropwise. The flocculated precipitate was filtered off and washed twice with distilled water; to the filtrate, 10 ml of 10% potassium cyanide, 4 ml of buffer solution and 1 g of ascorbic acid were added, and the volume was adjusted to 150 ml with distilled water. Four drops of indicator were added, and the magnesium was titrated with EDTA to a clear blue end-point. The end-point colour change was not as sharp as desired, so the EDTA was standardized (against pure magnesium sulphate) under the same lighting conditions, and with the same reagents present in solution. Pyrocatechol Violet, introduced by Suk

l.¹¹, was tried as an alternative indicator, but was considered inferior to Eriochrome black in this case.

Separations achieved in the column

Spectrographic examination of various fractions collected from the column in a number of runs, showed that during solvent elution:

In a few cases, small amounts of magnesium were found in the eluate (60–100 ml); in most cases, negligible amounts of magnesium passed out of the column.

Vanadium, titanium, and chromium were completely retained in the column.

Aluminium and nickel were retained almost completely in the cellulose; small amounts passed out in the 60–100 ml fraction.

Calcium was distributed between the eluate and the column.

Iron and manganese were completely removed from the column.

Notes on stages observed during solvent elution

A bright yellow-brown layer separated out on transfer of the sample to the tube; this band passed through the column, it was followed by a greenish-yellow zone; under ideal conditions, the solvent front appeared as a sharp line.

The bulk of the iron was removed with the first 40 ml of solvent; a thin blue-green line, rich in manganese, followed the iron, and was usually removed when 70 ml of solvent had passed through the column. With samples containing nickel, chromium, vanadium and vanadium, the eluted column had a pale brownish-yellow tint, more marked towards the top.

Marked changes in filtration rate were noted; while the main acid-rich fraction was being eluted, the rate dropped considerably; as the iron passed out of the column, the rate increased sharply; on elution with dilute acid, the filtration rate slowed again.

Removal of interfering ions before titration of magnesium

Spectrographic tests showed that there was no loss of magnesium in the ammonia precipitation step; the solution for titration contained only magnesium and nickel, with faint traces of calcium and aluminium.

RESULTS

Standards

Standard iron samples of known magnesium content were not available. Standards were made by additions of magnesium to solutions of pure iron (Adam Hilger Ltd. analysis: Mg 0.001%, Mn 0.1 p.p.m., Ni 0.0035%, Co 0.003%, Ca Nil). Blank tests were carried out on the pure iron and on the reagents. Results are shown in Table I.

TABLE I
RECOVERY OF MAGNESIUM FROM SYNTHETIC STANDARDS

Magnesium added mg	Magnesium found mg	Recovery %
Nil	Nil	—
1.10	1.10	100
0.55	0.56	102
0.55	0.55	100

TABLE II
ANALYSIS OF CAST IRON BY THE CHROMATOGRAPHIC SEPARATION METHOD

Sample	Magnesium found %			Mean %	Standard deviation %
1	0.026	0.027	0.028	0.029	7.9
	0.028	0.031	0.032		
	0.030	0.033	0.038		
2		0.039		0.035	11.4
	0.034	0.035	0.038		
	0.042	0.043			
3	0.055	0.053		0.054	—
4	0.052	0.055	0.060	0.058	9.1
		0.064			
5	0.060	0.068	0.074	0.070	11.3
		0.078			

Analysis of nodular cast iron

Six samples were examined by the new method and by other comparable rapid methods. The results are set out in the Tables II and III.

TABLE III
COMPARISON OF DIFFERENT METHODS FOR DETERMINATION OF MAGNESIUM

Method	% Mg found in sample					
	1	2	3	4	5	6
Chromatographic	0.029	0.035	0.038	0.054	0.058	0.070
Spectrographic	0.032	0.038	0.032	0.051	0.055	0.063
GREEN's method	—	0.044	0.041	0.064	0.058	0.058
(single determination only)						
REICHERT's method			— See Notes —			

Notes on Table III

1. Spectrographic analyses were made by a newly developed method¹², using a Hilger 3-metre grating spectrograph, and sparking solutions of iron on copper electrodes. Standards were prepared from pure iron rod and pure magnesium sulphate. The standard deviation of replicate analyses was approximately 5%.

2. GREEN's non-stoichiometric zinc oxide-ammonium persulphate separation method¹ was followed; the magnesium was titrated directly with EDTA, and no Tiron was added.

3. REICHERT's method³ using a single precipitation with ammonia and hydrogen sulphide to remove interfering metals before titration of magnesium with EDTA, was tried; satisfactory results were not obtained, as considerable quantities of magnesium appeared to be retained in the voluminous sulphide precipitate.

DISCUSSION

Chromatographic separation procedures are largely empirical, because of the interdependence of various parameters such as filtration rate, acidity gradients, maintenance of solvent equilibrium and complex formation. For efficient column operation, care in the packing and conditioning steps is essential; filtration rate should be controlled since too rapid a flow causes considerable "tailing off" of the iron zone.

Because standard samples of known magnesium content were not available, the accuracy of the method was not fully checked in this work, but in view of the good results with the synthetic standards, and the fair agreement with the spectrographic

work, it was considered that the method, although not highly reproducible, ($\pm 10\%$), might be acceptable for routine work, since results can be obtained quickly, with simple apparatus. Care in sampling test blocks is necessary, as YARNE AND SOBERS⁵ have shown that marked segregation of magnesium can occur.

The observed quantitative retention of titanium, chromium and vanadium in the column suggests further useful applications for the separation of traces of these elements.

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SUMMARY

Small amounts of magnesium present in solutions of cast iron can be separated by partition chromatography on cellulose columns. Magnesium may then be determined volumetrically. The method is rapid and gives results which appear acceptable for routine work. No elaborate apparatus is required.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage de petites quantités de magnésium dans une fonte. On effectue une séparation par chromatographie de partage sur colonnes de cellulose et on dose ensuite le magnésium par volumétrie.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Schnellbestimmung von Magnesium in Gusseisen. Die Trennung des Magnesiums erfolgt nach dem Prinzip der Verteilungschromatographie mit einer Cellulosekolonne. Das eluierte Magnesium wird anschliessend volumetrisch bestimmt.

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FACTORS AFFECTING THE ULTRAMICRO-DETERMINATION OF TRYPTOPHAN, KYNURENINE AND THEIR DERIVATIVES

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INTRODUCTION

In order to study the metabolic breakdown pathways of tryptophan, a technique is needed which can be adapted to the resolution of the by-products and to their quantitative determination. Paper chromatography and paper electrophoresis were investigated for possible use.

Fluorospectrophotometric methods have been investigated¹ in the microdetermination of certain fluorescing compounds, *i.e.*, tryptophan, kynurenine, anthranilic acid, etc., — in biological extracts and known solutions. These procedures are available when individual compounds are known to be present, but the presence of interfering compounds such as tryptophan derivatives or breakdown products limits their use and resolution is required before quantitative spectrophotometric analysis. The present investigation reports on the resolution and quantitative estimation of tryptophan and kynurenine from paper electrophoresis and paper chromatography.

The results obtained indicate that the electrolyte used in electrophoresis influences the mobility, the separation and the ultraviolet spectra of tryptophan and kynurenine. The pre-treatment of filter paper (see below) did not influence the R_F of tryptophan and kynurenine, but affected their quantitative determination. Elution of tryptophan or kynurenine from chromatograms or electrograms varied with the type of pH of the eluant. Unexpected interaction of kynurenine with certain electrolytes (phosphate and borate buffers used in electrophoresis) resulted in the appearance of at least two kynurenine derivatives.

Ultraviolet irradiation of either *l*- or *d*-tryptophan in aqueous solutions results in changes of their characteristic ultraviolet spectrum, and electrophoretic mobility. The pH of the solutions decreases and the solutions become colored with a faint odor.

EXPERIMENTAL

Materials

Whatman filter paper No. 1 was used. Three types of this filter were prepared: unwashed (as supplied by the manufacturer (A), washed with distilled water (B) and washed with 0.05N HCl (C). The amino acids *l*-tryptophan, *d*-tryptophan, *dl*-tryptophan, *l*-kynurenine, *d*-kynurenine and *dl*-kynurenine were all of the c.p. grade obtained from Mann Research Laboratories, and were purified so as to obtain chromatographically pure material. The optical rotation of each was checked before every experiment. All alcohols used were freshly distilled.

Chromatography

Tryptophan or kynurenine isomers were separated by paper chromatography. The solvent used consisted of equal volumes of 95 % ethanol and 0.1N acetic acid. The compounds were located by examining the chromatograms under ultraviolet

light. Tryptophans gave purple fluorescence, while kynurenines gave orange fluorescence when the dried chromatograms were examined without further treatment. After spraying the paper with 1M KCN, drying and re-examining under ultraviolet light, both tryptophan and kynurenine remained visible. After exposure to KCN, drying and spraying with Ehrlich reagent, tryptophan and kynurenine each produced a characteristic color.

Chromatograms sprayed with ninhydrin or Ehrlich reagent were used to locate tryptophan or kynurenine on unstained chromatograms. From duplicate untreated chromatograms, triangular wedges containing the located amino acids were cut out. The material was concentrated at the pointed tip of the wedge by dipping the broad side of the triangle in distilled water². After concentration, the pointed end of each wedge was cut and carefully placed on an already equilibrated paper electrophoresis apparatus.

Paper electrophoresis

Electrophoresis was performed in a type LKB 3276 electrophoresis apparatus, using 20×40 Schleicher and Schull No. 2043B filter paper, or in an electrophoresis apparatus as described earlier³. The following buffer systems were used: 0.2M phosphate buffers from pH 5.288–pH 8.043; 0.1M acetate buffers from pH 3.820–pH 5.120, and 0.1M borate buffer, pH 8.5. An average of 300 V potential and 0.05 mA current was used for a period of 10 h.

Ultraviolet spectrophotometric analysis

Compounds located on sprayed chromatograms were cut from duplicate untreated chromatograms and eluted in sterile distilled water, 0.05N HCl or NaOH–NaHCO₃.

RESULTS

Tryptophan and kynurenine were resolved by paper chromatography and paper electrophoresis, eluted and quantitatively determined. The behavior of tryptophan on paper chromatography was found to be influenced by the type or conditioning of the paper. Three types of filter paper were used: (A, B, C, as above). Although on these three papers, tryptophan showed comparable R_F position and fluorescence, when examined under ultraviolet light, elution data and ultraviolet spectra were variable.

Washing the filter paper with distilled water altered its porosity and its tissue structure in such a way as to reduce the recovery of tryptophan in distilled water. Only 51% of tryptophan was recovered from paper B, while from A or C papers, 71% and 83% recovery was obtained respectively. In acidic eluants (0.05N HCl) tryptophan was recovered to the extent of 81, 76 and 83% from filter papers A, B and C. Using alkaline eluants (NaOH, NaHCO₃) 84 to 86% of tryptophan was recovered from the three types of filter paper.

Tryptophan, on paper electrophoresis, using neutral (phosphate buffer), alkaline (borate buffer), or acid (acetate buffer) moved as one component. The relative electromobility of tryptophan in the above three buffers was 1 : 7 : 7 in borate, phosphate and acetate respectively. Elution data showed variations (71 to 93%) in recovery, depending on the buffer used in electrophoresis and the eluant. The best

260 $m\mu$. Calculations of elution data varied according to the O. D. readings of either one of the major maxima. In general, calculations from the O. D. at 360 $m\mu$ were much higher than those at 230 $m\mu$. Our data indicates that the shorter wave length is more accurate for quantitative determinations. The differences (230–220 $m\mu$) varied with the pH of the eluant. It is reduced to a minimum at acidic pH's and is more pronounced in the alkaline range (Fig. 3). With acetate buffer, the O. D. of the buffer itself could obscure the difference.

TABLE I

KYNURENINE SPECTROPHOTOMETRIC CONSTANTS AT DIFFERENT pH VALUES

pH	O.D. ₂₃₀ -O.D. ₂₂₀	O.D. ₂₃₀ -O.D. ₂₇₅	O.D. ₂₃₀ -O.D. ₃₀₀	O.D. ₃₆₀ -O.D. ₃₈₀	O.D. ₃₆₀ -O.D. ₂₃₀
1.00(HCl)	0.210	0.83	1.173	0.165	0.20
1.00(H ₂ SO ₄)	0.204	0.77	0.852	0.117	0.177
2.2(HAc)	0.225	0.92	0.855	0.145	0.211
3.60	0.110	0.88	0.810	0.115	0.207
3.80	0.140	0.84	0.800	0.120	0.209
4.20	0.095	0.89	0.805	0.125	0.200
4.80	0.124	0.87	0.790	0.115	0.228
5.28	0.222	0.59	0.524	0.155	0.295
5.90	0.202	0.56	0.451	0.145	0.321
6.46	0.194	0.69	0.549	0.148	0.269
6.80	0.169	0.74	0.635	0.154	0.242
7.16	0.132	0.82	0.676	0.120	0.215
8.04	0.194	0.77	0.769	0.118	0.180
13.00	0.262	0.34	0.373	0.072	0.228

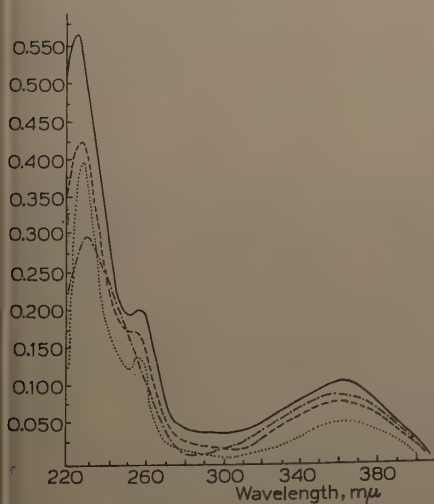


Fig. 3. Ultraviolet spectra of kynurenine. 1. Distilled water: —; 2. In 0.05N HCl: - - - -; 3. In 0.05N NaOH:; 4. In 0.05N H₂SO₄: (— · — · —)

TABLE II

TRYPTOPHAN SPECTROPHOTOMETRIC CONSTANTS AT DIFFERENT pH

pH	O.D. _{min} -O.D. _{max}	O.D. _{max} -O.D. _{min}
1.00(HCl)	0.360	0.390
1.00(H ₂ SO ₄)	0.370	0.391
2.20(HAc)	0.324	0.946
3.60	0.325	0.918
3.80	0.320	0.959
4.20	0.318	0.968
4.80	0.316	1.013
5.28	0.176	0.934
5.90	0.157	0.948
6.46	0.214	0.880
6.81	0.249	0.887
7.16	0.288	0.845
7.73	0.339	0.799
8.04	0.347	0.790
13.00	0.322	0.393

Variations in the constants of the spectral curve of kynurenine and tryptophan at different pH's are presented in Tables I and II. These variations indicate changes in the extinction coefficient of kynurenine and tryptophan exposed to these different pH conditions. These changes were brought about by the effect of salt concentration, hydrogen-ion concentration and conductivity of the electrolyte used.

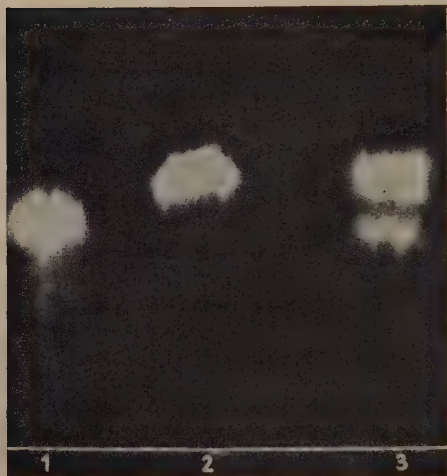


Fig. 4. Resolution of tryptophan isomers on paper chromatography. Whatman No. 1 filter paper was developed with methanol-water solvent (9 : 1) for 48 h, dried and examined as described in text. 1. *l*-tryptophan; 2. *d*-tryptophan; 3. *dl*-tryptophan.



Fig. 5. Resolution of kynurenine isomers on paper chromatography. Whatman No. 1 filter paper was developed with methanol-water solvent (9 : 1) for 48 h, dried and examined as described in text. 1. *l*-kynurenine; 2. *d*-kynurenine; 3. *dl*-kynurenine.

Ultraviolet irradiation of d-, l-, or dl-tryptophan

Aqueous solutions containing *d*-, *l*-, or *dl*-tryptophan (0.5*M*) when irradiated by ultraviolet light produce breakdown of tryptophan. *d*-kynurenine (from *d*-tryptophan), *l*-kynurenine (from *l*-tryptophan) and *dl*-kynurenine (from *dl*-tryptophan) were identified among the breakdown products. Ultraviolet light results in a decreased pH of the aqueous solutions, and in changes of spectral characteristic curve of tryptophan. The solutions acquire a color and on standing at 0° in the refrigerator, a faint odor is produced.

A Mineralight model V-41, with short wave ultraviolet (2537 Å) six bar quartz tube and special short-wave filter producing 45 mW per square foot was used as a source of the ultraviolet light.

Figs. 4 and 5 are chromatograms developed in methanol-water (9 : 1) solvent, demonstrating the resolution of *d*-, *l*-, and *dl*-tryptophan as well as the resolution of *d*-, *l*-, and *dl*-kynurenine respectively.

Figs. 6a and 6b are chromatograms developed in the methanol-water solvent,

irradiated *d*-tryptophan, *d*-kynurenine being one of the products (Fig. 6a). *l*-tryptophan is converted into *l*-kynurenine by ultraviolet irradiation and is presented in Fig. 6b. The chemical identity of remaining products of irradiation was well as the effect of pH, ionic strength of the solutions on the rate of tryptophan breakdown, etc., will be reported in the near future.

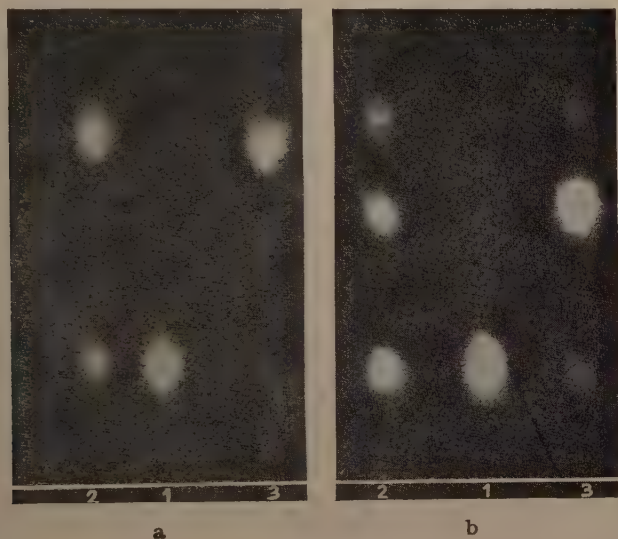


Fig. 6. (A) Action of ultraviolet light on *d*-tryptophan. A chromatogram developed in methanol-water solvent showing the conversion of *d*-tryptophan to *d*-kynurenine. 1. *d*-tryptophan; 2. *d*-tryptophan after ultraviolet irradiation (*i.e.*, *d*-kynurenine); 3. *d*-kynurenine (pure chemical). (B) Action of ultraviolet light on *l*-tryptophan. A chromatogram developed in methanol-water solvent showing the conversion of *l*-tryptophan to *l*-kynurenine. 1. *l*-tryptophan; 2. *l*-tryptophan after ultraviolet irradiation (*i.e.*, *l*-kynurenine); 3. *l*-kynurenine (pure chemical).

DISCUSSION

The resolution of *d*-, *l*-tryptophan and kynurenine on paper chromatography and paper electrophoresis is investigated. The resolution of the isomers of tryptophan and kynurenine is due to absorption of the amino acids on the surface of the optically activated cellulose of the filter paper. Such optical activation of cellulose could be induced by the specific chromatographic (organic) solvent used, *i.e.*, methanol.

Elution of tryptophan or kynurenine from chromatograms or electrograms varied with the pH of the eluant. The data obtained indicates that the best eluant for tryptophan and kynurenine from electrograms is either sterile distilled water or NaOH-NaHCO₃.

Using the ultraviolet spectrophotometric procedure described here in the determination of tryptophan and kynurenine, the data suggests that better determinations are obtained if the exact maximum wave length is used in calculation.

The nature of the chemical substances produced by the action of ultraviolet radiation on *d*-, *l*-, or *dl*-tryptophan, and on *d*-, *l*-, or *dl*-kynurenine indicates that tryptophan was degraded gradually into a series of products. The products identified from

the degradation of tryptophan are *d*-kynurenine (from *d*-tryptophan) and *l*-kynurenine (from *l*-tryptophan). Another product was identified in both tryptophan and kynurenine irradiated aqueous solutions. The kinetics of the reaction as well as the chemical identity of the resulting products are being studied.

Over recent years evidence has accumulated to emphasize the important role of radiation on many enzyme systems. In particular the radiation influence on certain hereditary material has been noted.

Several investigators⁴⁻⁶ have studied the action of x-rays on aqueous solutions of deoxyribonucleic acid and have observed physical effects such as a decrease in the viscosity of the solutions. SCHOLES *et al.*^{7,8} reported on the chemical effects of x-radiation on aqueous solutions of deoxyribonucleic acids and ribonucleic acids. The effect of radiation was interpreted as action of free radicals initiated by the action of the radiation on solvent in the following process⁹⁻¹¹:



SUMMARY

The factors affecting the ultramicrodetermination of tryptophan and kynurenine were investigated by paper electrophoresis, paper chromatography and spectrophotometry. The electrolyte used in electrophoresis influences the mobility, the separation and the ultraviolet spectra of tryptophan and kynurenine. The pre-treatment of filter paper for chromatography did not influence the R_F of tryptophan and kynurenine, but interfered with their quantitative determination. The effect of ultraviolet irradiation of *d*-, *l*-, and *dl*-tryptophan as well as *d*-, *l*-, and *dl*-kynurenine was studied.

RÉSUMÉ

Les facteurs intervenant lors de l'ultramicrodosage du tryptophane et de la kynurenine ont été examinés par électrophorèse sur papier, chromatographie sur papier et par spectrophotométrie.

ZUSAMMENFASSUNG

Die Faktoren, welche die Ultramikro-Bestimmung von Tryptophan und Kynurenin beeinflussen, wurden mit Hilfe der Papierelektrophorese, Papierchromatographie und Spektrophotometrie untersucht.

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SPECTROPHOTOMETRIC DETERMINATION OF LANTHANUM WITH NEO-THORONE

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INTRODUCTION

Although alizarin red S¹ is generally used as a colorimetric reagent for lanthanum, the colour reaction is not very sensitive, and other reagents such as hematoxylin² have also been applied.

In the present work, the thorium-complexing agent, 2-ortho-arsonophenyl-azo-2-(1,8-dihydroxynaphthalene-3,6-disulphonic acid)³, neo-thorone⁴⁻⁷, has been successfully utilized for direct spectrophotometric determination of microgram amounts of lanthanum. The method is based on the fact that lanthanum forms a reddish-violet water-soluble complex with neo-thorone which is stable in acidic or basic medium. The optimum conditions for the procedure are discussed below.

EXPERIMENTAL

Reagents

A solution of the pure sodium salt of 2-ortho-arsonophenyl-azo-2-(1,8-dioxynaphthalen-3,6-disulphonic acid) — neo-thorone — was prepared according to ISHIBASHI AND HIGASHI⁴. Neo-thorone (0.1 g) was dissolved in 100 ml of water.

A standard solution of lanthanum was prepared by dissolving 0.78 g of chemically pure lanthanum nitrate tetrahydrate (Merck's reagent) in distilled water and diluting to 250 ml. This solution containing 1.001 mg of lanthanum per ml was standardized gravimetrically as lanthanum oxide. It was diluted to give solutions containing μg -amounts of lanthanum per ml. All other chemicals used in this work were pure Merck's reagents.

Apparatus and technique

A Hitachi EPV-II spectrophotometer with cells of 1-cm path length was used for all measurements. All solutions were diluted to a final volume of 25 ml before transference to the absorption cells. The pH was measured with a Beckman H-2 type pH meter and adjusted by adding sodium acetate-acetic acid or ammonium chlorid-ammonia buffer solution.

RESULTS AND DISCUSSION

Absorption curves

Measured against a water blank, the absorption of the organic reagent (A in Fig. 1) and of a similar solution containing lanthanum (B in Fig. 1) indicated a shift of the absorption band towards longer wavelengths on the addition of lanthanum. The reagent plus lanthanum was measured against the solution of the reagent, B—A (C in Fig. 1). The predicted curve was obtained showing a maximum absorption at 570–575 $\text{m}\mu$. The data are plotted in Fig. 1.

Effect of various amounts of reagent

The absorption of a series of solutions of pH 9.0, each containing 52 μg of lanthanum

per 25 ml with varying amounts of reagent, was measured to determine a suitable concentration of the reagent. The results (Fig. 2) indicate that 2.0 ml of an aqueous 0.1% solution suffice to complex 0.05 mg of lanthanum in 25 ml of solution.

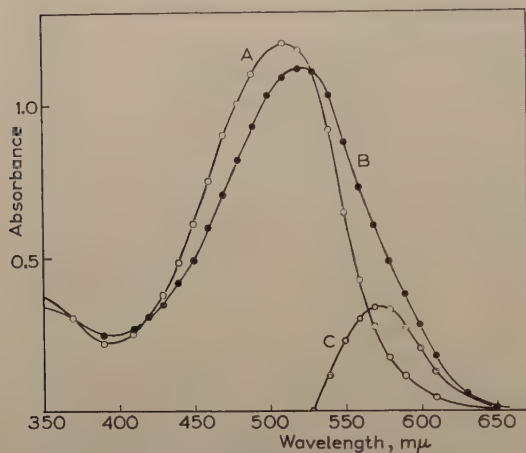


Fig. 1. Absorption spectra of neo-thorone; 25 ml final volume, Hitachi EPV-II spectrophotometer, slit width 0.05 mm. A: Reagent against water; B: Reagent plus lanthanum against water; C: Reagent plus lanthanum against reagent.

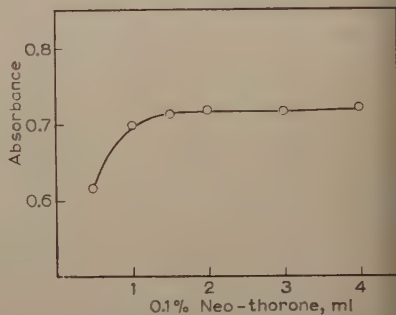


Fig. 2. Effect of neo-thorone concentration on absorbance; 52 μ g La taken, correction applied for blank.

Effect of pH

Solutions containing lanthanum and reagent were adjusted to various pH values with sodium acetate-acetic acid or ammonium chloride-ammonia buffer solutions. Between pH 8.0 and 9.0 the absorption remained approximately constant; above 9.0, it decreased rapidly (Fig. 3).

Effect of time, light and temperature

The colour of the lanthanum-neo-thorone complex in aqueous medium was fully developed after a few min, and the absorbance was unchanged for at least 4 h (Table I). Thus the system is sufficiently stable for quantitative determinations. The absorbance of the complex solution remained almost constant for 4 h under normal conditions of light and temperature (20–30°).

Beer's law

The coloured solution obeys Beer's law giving a standard curve, a straight line (see Fig. 4) passing through the origin with an absorbance of 0.684 for 50 μ g of lanthanum.

Sensitivity

The sensitivity of the colour reaction is either 0.008 μ g lanthanum per cm^2 (practical) or 0.0029 μ g lanthanum per cm^2 (according to SANDELL's definition).

TABLE I

VARIATION OF ABSORBANCE WITH TIME 2 ml OF 0.1% REAGENT IN WATER PLUS 15, 20, 25 μg OF LANTHANUM MEASURED *vs.* REAGENT AT pH 9.0, 570 $\text{m}\mu$

time min	absorbance		
	15 μg	20 μg	25 μg
15	0.210	0.280	0.350
45	0.208	0.275	0.347
75	0.208	0.275	0.347
105	0.208	0.275	0.348
130	0.207	0.275	0.345
240	0.207	0.275	0.347

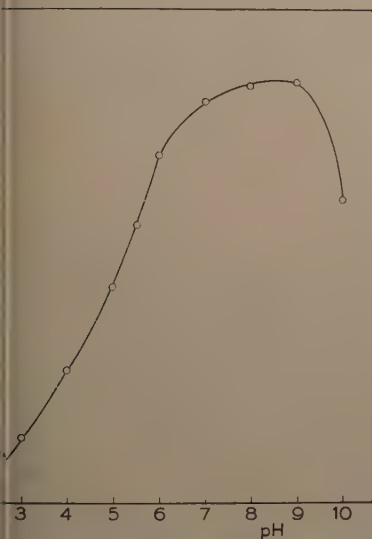


Fig. 3. Variation of absorbance with pH.

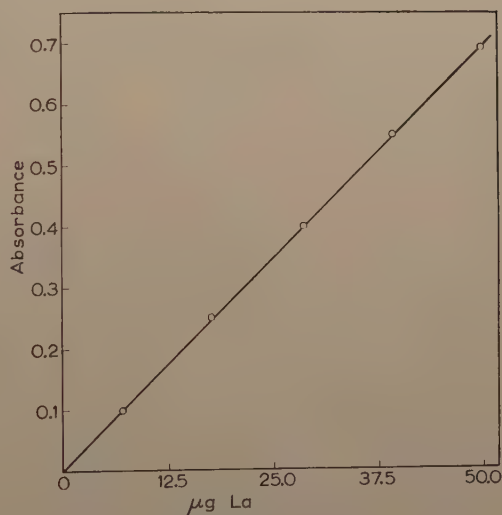


Fig. 4. Beer's law.

Experimental procedure

Aliquots of 0.5, 1.0, 1.5, . . . 5 ml of standard solution containing 10 μg of lanthanum . . . ml, were pipetted into 25-ml volumetric flasks. To each flask 5 ml of pH 9.0 buffer solution and 2 ml of 0.1% neo-thorone solution were added. The solutions were diluted to 25 ml with distilled water. A reference solution was prepared with reagent. The samples were then transferred to the absorption cells, and their absorbances were measured in a Hitachi EPV-II spectrophotometer.

Interferences

The effects of nearly all the elements associated with lanthanum were studied to determine their behaviour with neo-thorone under the optimum conditions used above. Citric and tartaric acids, oxalate, phosphate, and perchlorate even in minute amounts, interfered with the colour development.

Up to 400 μg of fluoride and up to 50 mg of acetate, sulfate, chloride and nitrate, as their sodium, potassium, or ammonium salts, did not interfere.

Many cations, *e.g.* aluminium, copper, iron(III), thorium, cerium and uranium, interfered by forming complexes with neo-thorone.

Studies on the separation of lanthanum from the interfering substances will be published later.

Composition of the coloured complex of lanthanum-neo-thorone

The empirical formula of the coloured complex of lanthanum was determined by adopting the "continuous variation" and "mole ratio" methods. Absorbance measurements at the wavelength of maximum absorption for the lanthanum complex were made within 5 minutes of preparing the solutions. Within experimental error, the results (Figs. 5 and 6) suggest a 1 : 3 complex of lanthanum with the reagent.

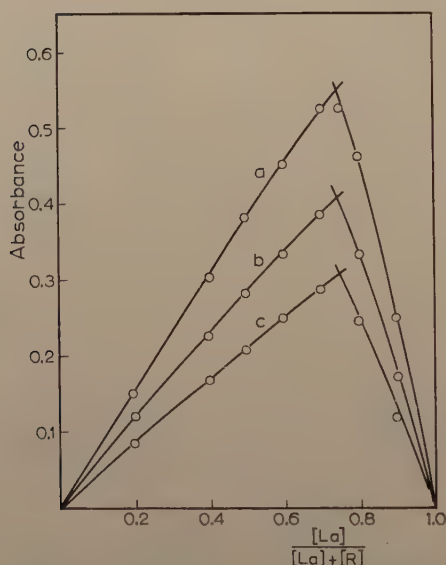


Fig. 5. Continuous variation method: reddish-violet complex of lanthanum and neo-thorone, pH 9.0, a. 570 m μ , b. 590 m μ , c. 600 m μ , $[R] = [La] = 1.74 \cdot 10^{-4} M$.

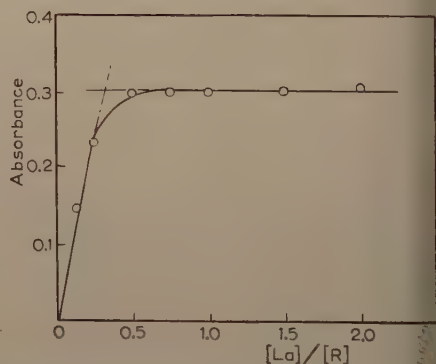


Fig. 6. Mole-ratio method; pH 9.0, 570 m μ , $[R] = [La] 1.74 \cdot 10^{-4} M$

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Prof. M. ISHIBASHI of the Kyoto university for his kind advice.

SUMMARY

A method has been developed for the spectrophotometric determination of microgram amounts of lanthanum by means of neo-thorone, 2-ortho-arsonophenyl-azo-2-(1,8-dioxynaphthalen-3,6-disulphonic acid). The method is sensitive, and as little as 2 μg of lanthanum can be determined in 25 ml of final volume. The calibration curve conforms to Beer's law. The stoichiometric composition of the coloured complex has been determined.

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RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du lanthane au moyen du néo-oron, acide arsonophényl-2-azo-2(dihydroxy-1,8-naphtalène disulfonique-3,6). Ce procédé est sensible et permet de doser jusqu'à 2 µg de lanthane dans 25 ml. La composition stoechiométrique complexe a été déterminée.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Lanthan mit Hilfe von „Neothoron“, 2-ortho-arsenophenyl-azo-2 (1.8-dioxynaphtalen-3.6-disulfosäure). Diese Reaktion erlaubt die Bestimmung von 2 µg Lanthan in 25 ml Lösung. Die stöchiometrische Zusammensetzung des gefärbten Komplexes wird angegeben.

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SUR LE DOSAGE DU CHROME DANS LES PRODUITS DE L'INDUSTRIE DU CIMENT

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INTRODUCTION

Dans un mémoire publié en 1950, JAEGER ET PELLONI¹ ont indiqué que les personnes atteintes d'eczéma au ciment réagissent positivement au test épicutané au chromate de potassium. Cette observation a amené ces auteurs à admettre que l'eczéma au ciment n'est pas causé par la basicité du ciment, comme on l'avait supposé auparavant, mais qu'il est dû à la présence de chromates dans les ciments. À la suite de ces constatations, nous avons examiné un certain nombre de ciments avec vue de déceler des traces de chromates. La plupart des produits analysés ont donné l'effet des réactions positives. Une orientation sur l'ordre de grandeur de la teneur en chromate nous a montré que les ciments contiennent en général quelques millièmes de Cr(VI), donc quelques mg Cr(VI) par kg de ciment sous forme d'anion CrO_4^{2-} soluble dans l'eau.

Il était important d'établir l'origine de l'élément chrome contenu dans les ciments. Certains auteurs ont admis que les traces de chrome proviennent de l'usure des appareils en acier chromé utilisés dans la fabrication du ciment (concasseurs, broyeurs, etc.). D'autre part, il fallait envisager la présence de chrome dans les matières premières servant à la fabrication du ciment.

Pour trancher la question, il était nécessaire d'élaborer des méthodes d'analyse

permettant de doser de très faibles quantités de chrome dans les diverses matières utilisées pour la fabrication du ciment. Ces méthodes concernent :

- A. le dosage du chrome total,
- B. le dosage du chrome hexavalent (anion CrO_4^{-2}).

A. DOSAGE DU CHROME TOTAL

Pour l'identification de l'anion chromate, on utilise couramment la diphénylcarbazide



qui donne avec le CrO_4^{-2} , en milieu acide, une coloration violette intense². Cette réaction est très sensible; elle se prête non seulement à l'identification du chromate, mais aussi au microdosage du chrome^{3,4}.

Nous avons appliqué cette réaction pour doser des traces de chrome dans l'oxyde de titane⁵ et pour déterminer la teneur en chrome des rubis⁶.

Le dosage du chrome total dans les produits employés et fabriqués par l'industrie du ciment comprend les opérations suivantes :

- I. Désagrégation de la matière à analyser
- II. Oxydation du Cr(III) en Cr(VI)
- III. Dosage colorimétrique de l'anion CrO_4^{-2} .

Nous avons examiné plusieurs procédés de désagrégation en vue de trouver une méthode appropriée pour solubiliser les ciments et les matières premières utilisées pour leur fabrication^{7,8}. Dans une étude se rapportant à la préparation et l'analyse du corindon⁶, nous avons reconnu les grands avantages que présentent des désagré-gations par fusion avec du borax. Cette méthode convient également pour solubiliser les produits de l'industrie du ciment. Le mode opératoire est indiqué ci-dessous.

Les essais qui visaient l'oxydation du Cr(III) en Cr(VI) par une fusion oxydante n'ont pas donné de résultats satisfaisants. Nous avons constaté qu'il est préférable d'oxyder le Cr(III), après solubilisation, par l'addition de persulfate de potassium et de nitrate d'argent, ce dernier sel agissant comme catalyseur.

L'anion CrO_4^{-2} obtenu de cette manière est dosé colorimétriquement après addition de diphénylcarbazide en milieu sulfurique. Cette dernière opération est délicate, car la coloration violette que donne le réactif n'est pas stable. Nous disposions d'un colorimètre Klett-Summerson qui convient parfaitement à ce genre de dosages.

A la suite de nombreux essais que nous avons exécuté, nous avons adopté le mode opératoire suivant pour le dosage du chrome total dans le ciment.

I. Désagrégation

Une prise d'env. 0,5 g de matière à analyser (ciment ou autre matière finement pulvérisée) est introduite dans un creuset de platine. On calcine à 800–900° au Teclu ou au four électrique pendant 20 à 30 min pour détruire les matières organiques qui peuvent se trouver dans le produit.

Après refroidissement, on ajoute 5 g de borax anhyde $\text{Na}_2\text{B}_4\text{O}_7$. (Le produit commercial „borax fondu” est pilé préalablement dans un mortier de porcelaine.) Le ciment et le fondant sont intimement mélangés. On chauffe sur Teclu jusqu'à fusion complète du borax, puis on agite légèrement le creuset pour homogénéiser son contenu

On calcine fortement pendant env. 1 h (pleine flamme du Teclu ou four électrique, température env. 900°).

On retire le creuset du four et, par un mouvement giratoire, on provoque la solidification de la masse en couche mince sur la paroi du creuset. (Il faut éviter la formation d'un bloc compact qui détériorerait le creuset.)

Après refroidissement, on introduit le creuset dans un bécher contenant env. 250 ml de H_2SO_4 2 N. On chauffe au bain-marie pendant env. 8 h (ou une nuit). Le produit de désagrégation étant dissous, on retire le creuset et on le rince avec quelques ml d'eau distillée.

7. Oxydation

On ajoute à la solution sulfurique de la désagrégation 3 ml de AgNO_3 0.1 N et 5 g de $\text{K}_2\text{S}_2\text{O}_8$ et on abandonne au bain-marie pendant 20–30 min.

On laisse refroidir, puis on neutralise par NH_3 conc. jusqu'à pH 7–9.

Remarque: Une coloration violette provient de l'oxydation du Mn^{+2} en MnO_4^- . Elle disparaît pendant l'opération qui suit.

Il y a précipitation de $\text{Fe}(\text{OH})_3 + \text{Al}(\text{OH})_3$. On chauffe au bain-marie pour coaguler précipité et on évapore jusqu'à un volume d'env. 150 ml. Après refroidissement, on filtre en recueillant le filtrat directement dans un ballon jaugé de 250 ml. On lave avec de l'eau distillée et on neutralise par H_2SO_4 2 N; finalement on acidifie la solution par 25 ml de H_2SO_4 2 N et on complète au trait de jauge avec de l'eau distillée. Pour le dosage colorimétrique, il faut que l'acidité de la solution soit 0.2 N.)

II. Dosage colorimétrique de l'anion CrO_4^{-2}

On utilise pour l'étalonnage des solutions standard de $\text{K}_2\text{Cr}_2\text{O}_7$.

Solution standard A: 0.566 g $\text{K}_2\text{Cr}_2\text{O}_7$ par l (1 ml contient 200 μg Cr).

Solution standard B: 0.0283 g $\text{K}_2\text{Cr}_2\text{O}_7$ par l (1 ml contient 10 μg Cr).

La solution B n'est pas stable; elle se prépare au moment de l'emploi par dilution de la solution A dans la proportion 1 : 20.

Pour le dosage du CrO_4^{-2} dans la solution obtenue sous II, on prélève d'abord une aliquote de solution (par exemple 10 ml) pour établir au colorimètre la „valeur à blanc” de la solution.

On ajoute au restant de la solution contenue dans le ballon jaugé 4 ml de diphénylcarbazine.

Préparation du réactif: On dissout 0.25 g de diphénylcarbazine dans 50 ml d'acétone, puis on complète à 100 ml par de l'eau. Cette solution ne se conserve pas, il faut donc toujours utiliser une solution fraîche préparée le jour de l'emploi.

La coloration violette provenant de l'action de la diphénylcarbazine sur l'anion CrO_4^{-2} se développe lentement. Elle atteint son maximum après env. 10 min.

L'analyse colorimétrique, qui doit se faire 10–15 min après l'addition du réactif, donne la quantité de Cr(VI) par ml de solution.

On obtient la teneur en chrome de la prise soumise à l'analyse en multipliant le résultat par 254 (volume de la solution 250 ml + réactif 4 ml).

Remarques:

1. Pour obtenir des résultats corrects, il est nécessaire de faire le dosage colori-

métrique le plus rapidement possible après l'acidification du filtrat ammoniacal (maximum admissible 30 min).

2. Pour toutes les opérations, on doit utiliser de l'eau distillée exempte de matières réductrices. (Distiller l'eau en présence d'un peu de KMnO_4 .) L'acide sulfurique est débarrassé de matières réductrices par chauffage jusqu'à dégagement de vapeurs blanches épaisses.

3. La méthode indiquée ci-dessus permet de doser le chrome avec une précision relative de quelques %. Il arrive que certains dosages donnent des résultats inexacts, sans qu'on puisse en indiquer les causes. C'est pourquoi nous faisons toujours au moins 3 dosages pour chaque produit. Si un des résultats s'écarte de plus de 5 % de la moyenne, ils est recommandé de refaire l'analyse avec de nouvelles prises.

B. DOSAGE DU CHROMATE SOLUBLE DANS LE CIMENT ET LE CLINKER

Nous nous sommes rendu compte que les matières premières utilisées pour la fabrication du ciment ne renferment pas de chrome hexavalent; par contre, on y trouve des quantités appréciables de chrome trivalent.

L'anion chromate se forme pendant la cuisson. Il a été constaté que les ciments fabriqués au four rotatif contiennent en général nettement plus de chromate que les ciments des fours à cuve.

Les ciments peuvent contenir, à côté de constituants oxydants (tel que l'anion CrO_4^{-2}), certaines matières réductrices. Si ces dernières sont solubles dans l'eau, elles peuvent provoquer des perturbations lors du dosage du chrome hexavalent dans l'extrait aqueux. Les diverses variantes que nous indiquons ci-dessous pour le dosage de l'anion chromate dans les ciments et les clinkers peuvent, par conséquent, donner des résultats différents.

Nous considérons le résultat le plus élevé que donne l'une des méthodes comme valeur la plus probable de la teneur en chromate.

Méthode I

Une prise de 15 à 20 g de ciment est introduite dans un ballon Stohmann contenant env. 250 ml d'eau distillée exempte de matières réductrices. On agite pour obtenir une suspension homogène, on complète avec de l'eau jusqu'au trait de jauge (500 ml) et on fait tourner le ballon Stohmann dans l'agitateur selon WAGNER pendant env. 20 min (20 tours par min).

Après décantation, on dose l'anion chromate dans une prise aliquote de la solution limpide.

Exemple: Prélever 25 ml dans un ballon jaugé de 100 ml, neutraliser avec H_2SO_4 2 N, puis acidifier avec 10 ml H_2SO_4 2 N; ajouter 2 ml de diphénylcarbazide et compléter à 100 ml avec de l'eau. Dosage colorimétrique après 10 min.

Méthode II (variante de la méthode I)

On extrait le chromate comme sous I, mais au lieu de laisser décanter, on filtre immédiatement sur filtre plissé.

A une prise aliquote du filtrat (par exemple 25 ml), on ajoute d'abord 2 ml de diphénylcarbazide, ensuite, par petites portions, H_2SO_4 N jusqu'à réaction acide. On dilue à 100 ml et on dose le chromate colorimétriquement.

Méthode III

Dans un bécher de 100 ml contenant une prise de 50 g de ciment on ajoute, à l'aide d'une pipette, 30 ml d'eau. On agite avec une baguette de verre jusqu'à ce qu'on obtienne une pâte homogène, puis on laisse reposer 10 min. On fait couler la pâte sur un entonnoir en porcelaine et on filtre sous vide (filtre quantitatif, bande bleue) sans perturber le précipité.

Dans une prise du filtrat, on dose le CrO_4^{2-} colorimétriquement après addition de H_2SO_4 et de diphénylcarbazide.

Remarque: La méthode III donne souvent des résultats légèrement plus faibles que la méthode I.

Méthode IV (variante de la méthode III)

On garnit un entonnoir de porcelaine (\varnothing env. 4-6 cm) avec un papier filtre (bande bleue) humidifié avec un peu d'eau. On introduit une prise de ciment de 20 à 30 g qu'on répartit en une couche d'égale épaisseur. On verse soigneusement 25 ml d'eau décaillée sur le ciment, puis on fait actionner la trompe à vide. Pendant cette opération, on laisse tomber de l'eau goutte à goutte sur le ciment.

TABLEAU I
EXEMPLES DE DOSAGES DE CHROME

	Chrome total mg Cr/kg	Chrome hexavalent mg Cr(VI)/kg	
		méthode I	méthode III
Ciment I provenant d'un four statif (ciment de composition courante)	54	7.2	5.9
	54	7.4 moy. 7.4	6.0 moy. 6.0
	56	7.5	6.0
	56 moy. 56	7.5	
	56		
	58		
Ciment II provenant d'un four statif (ciment particulièrement riche en chromate)	87	22.2	16.8
	87	22.2 moy. 22.2	16.9 moy. 17.0
	91 moy. 90	22.2	17.2
	92		
	93		
Ciment III provenant d'un four à cuve	53	1.8	1.6 moy. 1.7
	54 moy. 54	2.0 moy. 2.0	
	56	2.1	
Ciment calcaire	13		
	13 moy. 14		
	14		
	15		
Marne I (composition courante)	101		
	101 moy. 102		
	102		
	104		
Marne II (particulièrement riche en Cr)	253		
	253 moy. 258		
	260		
	265		

Avec 100 ml d'eau, on arrive ainsi à extraire pratiquement tout le chromate contenu dans le ciment. Dans cet extrait, on dose l'anion CrO_4^{-2} en ajoutant, à une prise aliquote, d'abord la diphénylcarbazine et ensuite H_2SO_4 2 N (comme méthode II).

Remarque. Le méthode IV convient particulièrement à la recherche et au dosage du chromate dans les ciments provenant de fours à cuve. Nous avons constaté que ces ciments renferment des réducteurs, par exemple l'anion sulfure, qui réduisent le Cr(VI) en Cr(III). La méthode IV offre les meilleures chances d'éviter ces perturbations. Il nous est arrivé que certains ciments donnaient des résultats négatifs pour la teneur en CrO_4^{-2} selon les méthodes I, II et III, mais indiquaient bien la présence de CrO_4^{-2} lorsqu'on opérait selon la méthode IV.

REMERCIEMENTS

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RÉSUMÉ

Pour le dosage de très faibles quantités de chrome dans les ciments et dans les matières premières servant à leur fabrication, les auteurs proposent une méthode qui comprend les opérations suivantes: Désagréation par fusion avec du borax anhydre, dissolution de la masse de désagréation dans H_2SO_4 dilué et oxydation du Cr(III) en Cr(VI) par $\text{K}_2\text{S}_2\text{O}_8 + \text{AgNO}_3$, précipitation du fer et de l'aluminium par addition de NH_3 , dosage colorimétrique de l'anion CrO_4^{-2} en milieu sulfurique au moyen de la diphénylcarbazine.

Les ciments et les clinkers contiennent du chrome hexavalent sous forme d'anion CrO_4^{-2} soluble dans l'eau. Le dosage de CrO_4^{-2} se fait par colorimétrie dans l'extrait aqueux. Quatre méthodes d'extraction sont indiquées. La présence de matières réductrices dans les ciments peut provoquer des perturbations.

SUMMARY

A method is described for the determination of small amounts of chromium in cement. The cement is decomposed by fusion with borax and the chromium is converted into chromate. Upon addition of diphenyl-carbazide, a coloured complex is obtained, which can be determined colorimetrically.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung kleiner Mengen Chrom in Zement durch Aufschluss mit Borax und Überführung des Chrom-(3) in Chromat. Dieses gibt mit Diphenylcarbazon eine gefärbte Komplexverbindung, die kolorimetrisch bestimmt wird.

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ELECTRON TRANSFER SPECTRA IN COPPER AMMINES

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When the measurement of the absorption spectra of inorganic salts is extended into the ultraviolet, an intense absorption-band is noticed in the region of $200\text{ m}\mu$. In the case of transition metal ions the UV-band is several thousand times more intense than the visible band. These spectra are associated with the transfer of an electron between the ion and a water molecule in the hydration sphere, and have been named electron transfer spectra. For such a process to occur with reasonable probability, the two atoms must be bound together by comparatively strong forces, but the bonding must not interfere with the assignment of electrons to individual atoms, *i.e.*, the bonds must be of ionic or ion-dipole character rather than true atomic (electron-pair) bonds. The stronger the bond, the more energy is necessary to bring about an electron-transfer, and hence the absorption band appears at a shorter wavelength with stronger bonds.

The stable alkali and alkaline earth metal ions do not show any electron transfer band below the limit of observation in the usual spectrophotometer. The hydrated ions of other metals have been thoroughly studied by FROMHERZ *et al.*²⁻⁴ and show fairly strong electron transfer bands. There is a large class of complex compounds in which the water molecules of the hydrates are replaced by other neutral molecules, particularly ammonia and amines. It was expected that the amines would show electron transfer bands of considerable intensity in the UV-region, but as amines are stabler than the hydrates, these bands would probably be located at shorter wavelengths than in the hydrates. This is probably the reason why no systematic study of the electron transfer spectra of metal amines has been reported.

It is known that in the case of metal amines all the ammonia molecules are not bound to the metal ion equally strongly⁵. Particularly, in the case of copper hexamine two of the ammonia molecules are weakly bound and it is even doubtful if hexamine can exist in solution at all. It was surmised that the electron transfer bands would be located at longer wavelengths than the corresponding hydrates. To study this problem, the absorption spectra of a number of copper amines were measured in the range of $200\text{--}250\text{ m}\mu$.

EXPERIMENTAL

E. Merck's G.R. quality reagents were used in all these measurements. The solvents were scrupulously purified to make them transparent in the region $200\text{--}250\text{ m}\mu$. The absorption spectra measurements were made in Hilger UV-speck and Beckman Spectrophotometer Model DU, using 1-cm matched silica cells.

DISCUSSION

An equilibrium between tetra, penta and hexammines may exist in the solution hence its composition was uncertain and the extinction values had to be expressed in terms of the copper concentration rather than that of the complex. It was found that on that basis the extinction of the UV-bands shown in Fig. 1 was 6,000 to 14,000 times more intense than the visible band of copper at $790\text{ m}\mu$.

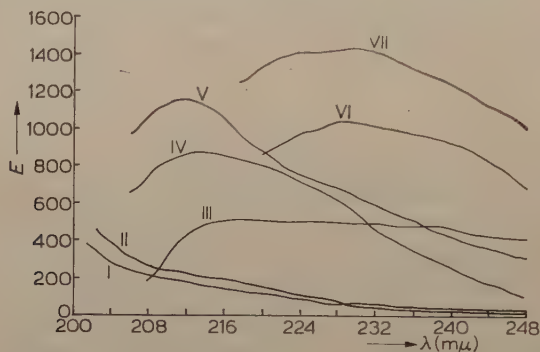


Fig. 1. Absorption spectra of copper amines in the UV-region. Curve I: copper acetate (copper conc. $10^{-3} M$); curve II: copper perchlorate (copper conc. $10^{-3} M$); curve III: copper perchlorate- $0.5 M$ methyl ammine (copper conc. $10^{-4} M$); curve IV: copper perchlorate- $0.5 M$ ammonia- $0.5 M$ ammonium sulphate (copper conc. $10^{-4} M$); curve V: copper perchlorate- $0.5 M$ ammonia (copper conc. $10^{-4} M$); curve VI: copper perchlorate- $0.5 M$ ethylene diamine (copper conc. $10^{-4} M$); curve VII: copper glycinate (copper conc. $10^{-4} M$).

In order to suppress anion association copper was used as its perchlorate. In the case of amines the ammonia concentration was at least 100 times that of copper to ensure the presence of copper in its highest coordination state. It can be seen from curves II and V that the ammine showed an absorption band at about $214\text{ m}\mu$, while the band for hydrate was located somewhere below $200\text{ m}\mu$. When ammonium sulphate was added to the solution of copper ammine, the band became diffuse and extinction was suppressed, but the peak appeared at about the same position. In the case of methylamine the band was broad and diffuse, extending from 212 – $240\text{ m}\mu$. With ethylenediamine the peak of the band shifted to $228\text{ m}\mu$, but the extinction was of the same order of magnitude as the simple ammine. The shape of the band suggests that actually two bands with peaks at $228\text{ m}\mu$ and $234\text{ m}\mu$ respectively were superimposed. Probably the two bands are associated with the cis- and trans-modifications of copper ethylene diamine dihydrate. In the case of amines a similar difference between the cis- and trans-forms would be expected, but their sharpness is probably lost because of the superposition of penta- and hexamine bands.

In the case of copper glycinate the characteristic absorption band was found to be a superposition of two bands with peaks at $222\text{ m}\mu$ and $230\text{ m}\mu$. In this case the electron transfer may take place between the copper and the amino or carboxyl groups of the glycine molecule. The absorption spectra of copper acetate in this region showed no peak and the extinction over the whole region was extremely low, indicating the absence of electron transfer between copper and carboxyl groups. It may be concluded that in glycinate the electron transfer takes place between copper and the amino groups.

Most of the amines can exist as hydrates in solution and the water molecules in these hydrates are much less tightly bound than in simple hydrates. The electron transfer observed may be between the metal ion and the water molecule in the coordination sphere rather than between the metal and the ammine group. It has been shown by DAINTON AND JAMES⁶ that in the case of hydrates the electron transfer actually takes place from the metal to the water molecule. The H_2O^- formed decomposes to give H atoms, whose existence may be proved by the initiation of polymerisation of acrylonitrile. When an aqueous solution of acrylonitrile containing the copper ammine was irradiated with light of a wavelength corresponding to the peak of the characteristic absorption band, no polymerisation took place. This probably means that the electron transfer bands are not due to transition between metal and water but to transfer between metal and ammine group. However, the polymerisation of acrylonitrile may be inhibited by the amines, so that the bands may actually be due to the former transition. It is difficult to reach a definite conclusion at this stage. It has been demonstrated that in aqueous ammoniacal solution copper may exist as a hydroxo complex, $[Cu(NH_3)_3(OH)(H_2O)_2]^+$, especially if the solution be weak in ammonia. The situation in this complex is similar to anion association and there may be a strong electron transfer band owing to transition between copper and hydroxyl groups. Possibly, the intense UV-bands reported above are due to similar hydroxo complexes of copper. The copper ammine in a solution containing less than 0.1 M ammonia showed an absorption band at 275 m μ which was about 200 times more intense than the visible band but only a fifth of that at 214 m μ . In 0.5 M ammonia solution the band at 275 m μ was absent. It can be concluded that the 275 m μ band is due to hydroxo compound, while the bands in the vicinity of 212–230 m μ are in fact genuine ammine bands.

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SUMMARY

The absorption spectra of ammine, ethylenediammine and methylamine complexes of copper as well as of copper glycinate in aqueous solution showed intense absorption bands in the region 200–250 m μ . These bands have been associated with the electron transfer spectra between the copper and the ammine group. No unequivocal assignment of the direction of electron transfer could be made.

RÉSUMÉ

Les auteurs ont effectué une étude des spectres d'absorption des composés: cuivre-ammines, cuivre-éthylènediammine, cuivre-méthylamine et glycinate de cuivre.

ZUSAMMENFASSUNG

Es wurden die Absorptionsspektren von Kupferamminen, Kupfer-äthylendiamminen, Kupfer-methylamminen und Kupferglycinat in wässriger Lösung gemessen.

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THE DETERMINATION OF CYSTINE WITH *p*-AMINODIMETHYLANILINE

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The formation of a blue colour in the reaction between cysteine and *p*-aminodimethylaniline in the presence of ferric ions was observed first by FLEMING¹ and later developed into a quantitative procedure for the determination of cystine by VASSEL². This method involves the reduction, in acid solution, of cystine to cysteine by zinc in the presence of the reagent and a ferric salt (which is also reduced); the colour is developed by adding an excess of ferric ions and heating. By reducing the cystine before the addition of the reagent and by using a larger quantity of zinc, MECHAM³ increased the sensitivity and improved the reproducibility of this determination.

The main disadvantage of these methods is that the reagent blanks are strongly coloured and absorb appreciably at the wavelength of maximum absorption of the blue compound.

In the present investigation it has been found that the blue compound is extracted completely on shaking with iso-amyl alcohol. The extract is contaminated with a small amount of a brown impurity, probably oxidised *p*-aminodimethylaniline, but this may be extracted from the alcohol solution by aqueous alkali. The blue compound, which is believed to be a carboxy-benzothiazine², assumes a more intense colour on being rendered alkaline. Strong bases, like sodium or potassium hydroxide, cause the colour to become more red and less intense than does ammonium hydroxide; another advantage in using the weaker base is that it has less tendency to emulsify the alcohol during extraction. The addition of ammonium chloride also assists in preventing the formation of an emulsion.

The optimum conditions for the formation of the blue compound have been re-investigated using this extraction technique. The test is not very sensitive to changes in the concentrations of zinc, ferric and ferrous ions and *p*-aminodimethylaniline over a wide range but is very dependent on acid concentration. The maximum development of the blue colour occurs at a much lower concentration of acid than that recommended by VASSEL and MECHAM who may have used an excess of acid to suppress the colour due to ferric salts.

The colour, measured at maximum absorption, is more stable than that produced by previous methods; during a period of 5 days at room temperature, a constant rate of fading of about 1% per day was observed; the colour produced by VASSEL's method increased by 40% during the same period under the same conditions. The intensity of the colour in amyl alcohol decreases slightly with increase in temperature (about 4% per 10°) and for accurate work, measurements should be made at the temperature used for the calibration tests.

MECHAM's reagent, which is prepared by reducing ferric ammonium sulphate with ascorbic acid in the presence of *p*-aminodimethylaniline, does not appear to have any advantage over the proposed reagent which is prepared directly from the ferrous salt and is stable for at least four weeks when stored in a brown glass bottle at room temperature. Fig. 1 compares the absorption spectra of the coloured solutions obtained by VASSEL's method (curve A), MECHAM's method (B) and the present method (D). Curve C shows the present method without the alkali treatment of the alcohol extract. In each case the same weight of cystine was used and the final volumes were the same; measurements were made against the respective reagent blanks. The absorption spectra of these reagent blanks measured against the respective pure solvents (Fig. 2) illustrate the almost complete elimination of extraneous colour in the present method. The results of twelve determinations performed on the same wool hydrolysate showed a maximum deviation from the mean of 0.4%. A series of tests in which

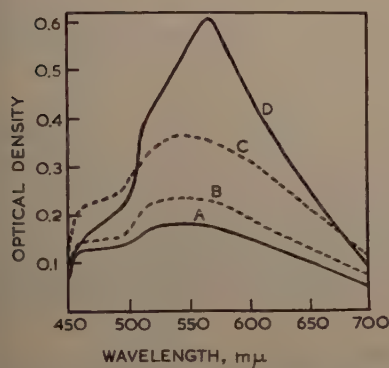


Fig. 1. Absorption spectra of test solutions measured against reagent blanks.

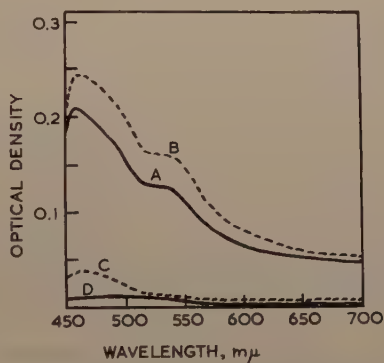


Fig. 2. Absorption spectra of reagent blanks measured against pure solvents.

known amounts of cystine were added to a cystine-containing protein hydrolysate gave results to within 1% of the calculated values. The proteins used for these tests were hydrolysed by refluxing with 6 *N* hydrochloric acid. VASSEL claimed that formic acid in the hydrolysing mixture increased the colour intensity but, under the present conditions, the increase obtained by replacing half of the hydrochloric acid by an equivalent amount of formic acid was very small.

A calibration curve may be prepared by using a solution of purified cystine in dilute hydrochloric acid.

Beer's Law remains valid up to 40 μg of cystine.

METHOD

Reagents

p-Aminodimethylaniline reagent. 24.0 g of $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ and 8.0 g of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ are dissolved in *N* H_2SO_4 and 0.04 g of *p*-aminodimethylaniline sulphate is added. The volume is made up to 100 ml with *N* H_2SO_4 .

Ferric ammonium sulphate. 20.0 g of $\text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24 \text{H}_2\text{O}$ is dissolved in *N* H_2SO_4 to give 100 ml of solution.

Ammonia/ammonium chloride reagent. 10.7 g of NH_4Cl and 11.2 ml of 0.880 ammonia solution are made up to 100 ml with water.

REDUCTION OF CYSTINE

5 ml of a protein hydrolysate, containing between 0.2 and 0.4 mg of cystine and approximately 1.1 *N* with respect to hydrochloric acid, is added to 5 ml of concentrated hydrochloric acid in a boiling tube. 0.3 g of zinc dust is added and a Kjeldahl stopper is placed in the tube immediately. The tube is shaken occasionally until all the zinc is dissolved; this usually requires about 30 min. The tilted tube is rotated to wash down the sides. Cysteine should be determined soon after the reduction is completed.

DETERMINATION OF CYSTEINE

1 ml of the reduced cystine solution is measured into a boiling tube; an accurately calibrated glass 'walking-stick' pipette (Gallenkamp) is convenient for this purpose as this type of pipette has been found to have an error of rather less than $\pm 0.1\%$. 5 ml of the *p*-aminodimethylaniline reagent is added immediately and the shaken mixture is allowed to stand for 4 min. 3 ml of the ferric ammonium sulphate solution is added and a Kjeldahl stopper is inserted into the neck of the boiling tube. The tube is immersed, to within 5 cm of the top, in vigorously boiling water for 50 min and then cooled in running water.

The resulting brown solution is extracted twice with 10 ml of iso-amyl alcohol and the combined organic layers are extracted twice with 10 ml of the ammonia/ammonium chloride reagent. Filtration of the separated alcohol solution through No. 1 Whatman paper produces a clear blue solution with a slight red fluorescence.

The colour is measured against a reagent blank (prepared by the same procedure except that 1.1 *N* hydrochloric acid is substituted for the hydrolysate) using an Ilford filter 626.

ACKNOWLEDGEMENT

I thank the Directors of A.R. Davis & Co. for permission to publish this paper.

SUMMARY

The considerable background colour in previous methods for the absorptiometric determination of cystine by means of *p*-aminodimethylaniline has been almost eliminated by solvent extraction of the required coloured compound. Alkali treatment of the extract intensifies the colour. The improved test is two and a half times more sensitive than previous tests based on the same reaction and the colour produced has a more sharply defined absorption peak. Cystine (plus cysteine) in protein hydrolysates may be determined with an error of less than 1%.

RÉSUMÉ

Les auteurs proposent d'effectuer une extraction à l'aide d'un solvant organique, lors du dosage absorptiométrique de la cystine au moyen de la *p*-aminodiméthylaniline. Cette modification permet d'améliorer considérablement la sensibilité de la méthode.

ZUSAMMENFASSUNG

Es wird eine Verbesserung der absorptiometrischen Methode zur Bestimmung von Cystin mit *p*-Aminodimethylanilin beschrieben. Durch Extraktion mit einem Lösungsmittel wird die Empfindlichkeit der Methode wesentlich erhöht.

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CONDUCTOMETRIC AND POTENTIOMETRIC TITRATIONS OF
NITROGEN BASES IN NON-AQUEOUS SOLVENTS

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INTRODUCTION

Nitrogen bases are in general determined quantitatively by titration in acidic solvents, the end-point being found either by the potentiometric method or by means of a colour indicator. In the former method solvents containing glacial acetic acid are commonly used¹, the inert balance being a compound such as benzene, chloroform, chloroform or a similar solvent. The use of completely inert solvents is restricted to the colour indicator method, because the input impedance of most potentiometers is too low for such poorly conducting systems.

The main disadvantage of acetic acid is its levelling effect on the strength of nitrogen bases and its small potential range. A consequence of the latter fact is that strong and weak nitrogen bases cannot be clearly distinguished from each other. Hence, in recent years efforts have been made to find more suitable solvents with a stronger differentiating capacity. Acetonitrile² and methyl isobutyl ketone³ have been among the solvents used; their potential range is 2 to 3 times that of acetic acid. Methyl isobutyl ketone as well as acetone⁴ can also be used for differentiating between acids of different strength.

The disadvantage of the use of solvents with keto groups for the titration of nitrogen bases is the possibility of a reaction between primary amines and the solvent to yield ketimines ($R_1R_2C = NR_3$), which results in low values in the determinations. The purpose of the present investigation was therefore to develop other wide-range solvents which do not react with the solutes or titrants employed. The search for these media was stimulated by the results obtained in the conductometric titration of dibasic acids, where the influence of factors like solvents, temperature, etc. was studied⁵. By analogy, the stress in the present work was laid on the determination of bivalent nitrogen bases, and the corresponding factors were considered, *viz.*:

The properties of the solvent, in particular: a. the solvating power (presence of groups forming hydrogen bonds, such as $-OH$), b. the mean dielectric constant. The dimensions of the acid anions, ClO_4^- versus Cl^- . (3) The distance between the basic groups and steric hindrance. (4) The temperature.

EXPERIMENTAL

Solvents and titrant solutions

The solvents generally used were methanol, propanol-2, nitrobenzene and binary mixtures of these with each other or with a hydrocarbon (benzene or *n*-heptane). All solvents were chemical grade and no special purification was applied. The water content was 0.3% or lower. The titrant solutions were 0.1 *N* perchloric and hydrochloric acid in dioxan. These reagents were

prepared in the usual way, *i.e.* by dilution of concentrated aqueous solutions with the organic solvent to the required strength. The dioxan was purified by drying on solid potassium hydroxide, followed by distillation over sodium.

Apparatus

(a) The conductometric titrations were performed with the aid of the a.c. Wheatstone bridge described previously⁵. The working frequency was 1000 c/s. The electrode system was a Philips dipping cell GM 4221, consisting of platinized platinum electrodes, with a cell constant of approx. 0.8.

(b) For the potentiometric determinations either the Electrofact Precision Laboratory pH/mV meter, type 6 C 30/2/KF or the Vibron Electrometer, model 33 B (Electronic Instruments Ltd.) was employed. The input impedance of the latter instrument is much higher than that of the Electrofact meter, $10^{13} \Omega$ as compared with $10^8 \Omega$. Hence the Vibron meter is especially suitable for poorly conducting solutions for which the Electrofact meter cannot be applied.

For all potentiometric titrations a glass-calomel electrode system was used, the latter electrode being filled with a saturated solution of potassium chloride in propanol-2. The glass electrodes were the Electrofact type 6 C 30/75, for use with the Electrofact meter, and the Beckman type 1190-90, for the Vibron meter.

It should be noted that although the absolute potential values indicated by the different combinations, millivoltmeter-glass electrode, were different, the potential range covered was, as a first approximation, independent of the type of the meter or of the glass electrodes. The titrations were performed in a cylindrical, jacketed glass vessel closed by a cork plug. This plug was provided with holes for the electrodes, a thermometer and the burette tip. Water from a thermostat circulating through the cell jacket permitted temperature control to $\pm 0.05^\circ$ at all temperatures used (25° , 50° and 75°). During titration the solution was stirred with a magnetic stirrer.

Titration procedure

For every titration 10 ml of a 0.01 *M* standard solution of the base was pipetted into the cell and diluted to a volume of 40–60 ml. The solution was stirred until it had attained the temperature of the thermostatted vessel. Small portions of titrant were added (approx. 0.10 ml from a semi-micro burette) and the readings were taken when they became constant. This was normally the case within half a minute.

TITRATION OF MONOVALENT BASES

The monovalent bases studied belonged to various groups, *viz.* aliphatic amines, anilines and heterocyclic basic nitrogen compounds.

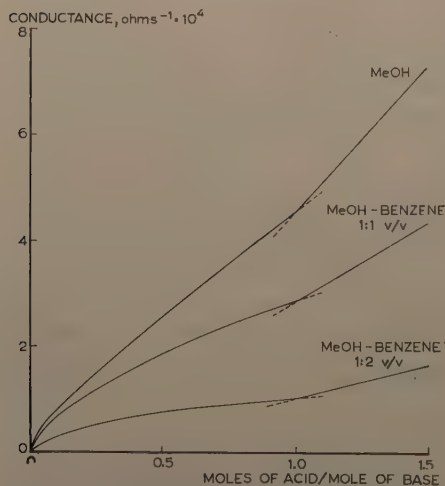


Fig. 1. Conductometric titration of piperidine in methanol-benzene mixtures with perchloric acid.

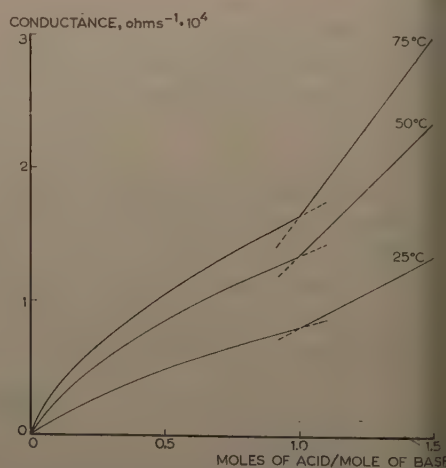


Fig. 2. Conductometric titration of diethanolamine in propanol-2 with perchloric acid at different temperatures.

In the conductometric titrations all monovalent bases gave similar curves when the same solvent was used. Consequently, a mixture of monovalent bases of different basicity cannot be differentiated in this way.

Increasing the volume fractions of hydrocarbon in the solvent methanol-benzene did not improve the sharpness of the equivalence point (Fig. 1), in contrast to raising the temperature (Fig. 2). Solvent mixtures mainly consisting of an indifferent compound such as nitrobenzene (to increase the conductance) and a small amount of methanol were unsuitable for conductometric titrations.

In the potentiometric titrations, however, this solvent system gave attractive titration curves. Optimum results were obtained both in pure nitrobenzene and in mixtures containing equal volume fractions of this solvent and dioxan or a hydrocarbon (see Fig. 4). Other solvents giving satisfactory curves were: methanol, ethanol, propanol-2 and mixtures of these alcohols with benzene (Fig. 3). From Fig. 3 it can be seen that the potential range increases in the order: propanol-2 < ethanol < methanol. (This order is valid both for the pure alcohols and for the alcohol-benzene mixtures.)

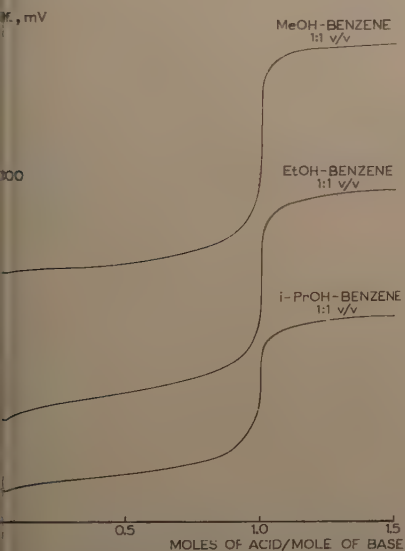


Fig. 3. Potentiometric titration of piperidine in different solvents with perchloric acid (curves have been shifted vertically for clarity).

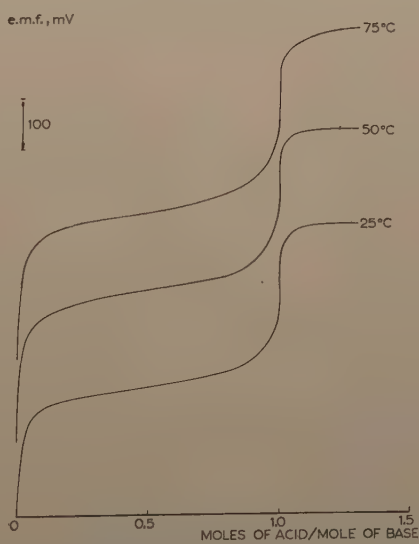


Fig. 4. Potentiometric titration of *p*-toluidine in nitrobenzene-xylene (1 : 1 v/v) with perchloric acid at different temperatures (curves have been shifted vertically for clarity).

Finally, the influence of temperature on the potentiometric titration of *p*-toluidine is shown in Fig. 4. The only effect is a possible small increase in the difference between half-neutralization potential (h.n.p.) and the final potential, *viz.* from approx. 300 mV at 25° to 350 mV at 75°.

TITRATION OF BIVALENT BASES

All the bivalent bases studied were either aliphatic or alicyclic, *viz.* members of the series of the α,ω -diamines and derivatives, and two diaminocyclohexanes.

With these bases special attention was paid to the four factors mentioned in the introduction, *viz.* properties of solvent, dimensions of acid anion, distance between the basic groups and temperature.

In this section we shall take the conductometric and the potentiometric titrations together and discuss the results in connection with the above-mentioned factors. Their influence is best illustrated by the experiments with the α,ω -diamines, including their derivatives.

Influence of solvent

For the solvents used the same restriction had to be made as for monovalent bases: nitrobenzene was in general unsuitable for the conductometric titrations and only alcohol-hydrocarbon mixtures were used. In potentiometry, on the other hand, solvent systems containing nitrobenzene gave the best results, just as with the monovalent bases.

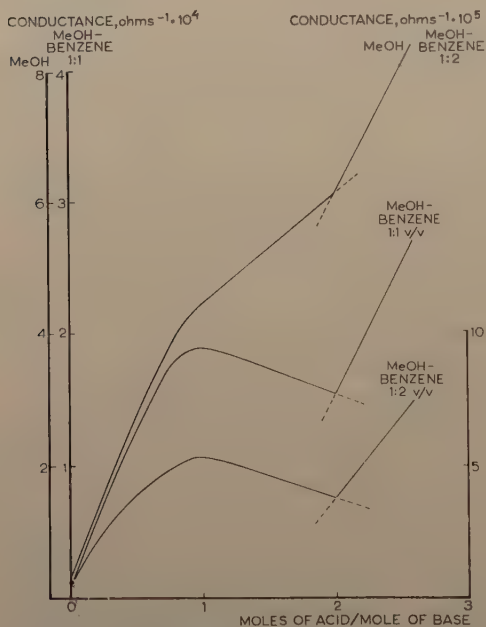


Fig. 5. Conductometric titration of ethylenediamine with perchloric acid in methanol-benzene mixtures.

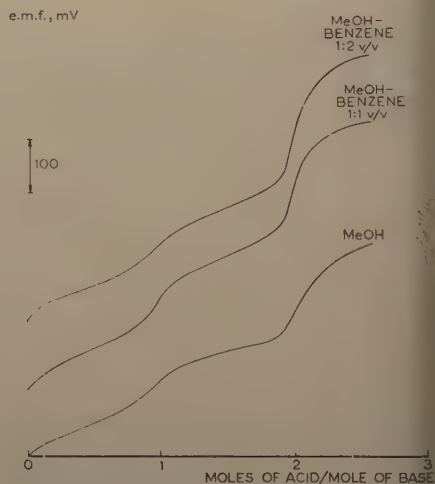


Fig. 6. Potentiometric titration of ethylenediamine with perchloric acid in methanol-benzene mixtures (curves have been shifted vertically for clarity).

Decreasing the dielectric constant, ϵ , of the solvent gave analogous results in conductometric titrations as previously reported for the dibasic acids⁵. The lower diamines showed more pronounced N-shaped titration curves (Fig. 5). In contrast to the results obtained with the dibasic acids the first equivalence point of the titration of bivalent amines could not be accurately determined in many cases. Consequently, application of conductometric analysis to mixtures of these compounds is somewhat restricted.

The influence of the dielectric constant on the shape of the curves was less pronounced in the potentiometric than in the conductometric titration (*cf.* Figs. 5 and 6). In general, the first potentiometric equivalence points in solvents containing methanol are also indistinct.

In the system methanol-benzene both the dielectric constant and the mean solvating power decrease when more benzene is used. Hence the ϵ effect and the solvation effect reinforce each other's influence on the properties of the solvent blend, but the former predominates⁵.

From the foregoing it can be seen that, although resolution of the two equivalence points is better in methanol-benzene mixtures than in the traditionally used glacial acetic acid, the former are not ideal.

Better results are obtained when the solvating power of the solvent is considerably decreased. The results of this modification are visible in both techniques, but most clearly so for the potentiometric titrations in solvents containing nitrobenzene. An illustration of the influence of the solvating power (at approximately constant dielectric constant) on the shape of the titration curve and hence on the resolving power of the solvent is given in Fig. 7. Here the curves have been slightly displaced, so that the second h.n.p. values coincide, but since the actual h.n.p.'s did not differ by more than 25 mV, this figure represents the true titration curves very satisfactorily.

From this result we see that:

The upper (acidic) limit of the potentials in nitrobenzene is rather sensitive to the presence of methanol (and other strongly solvating solvents). The influence of the alcohol, however, is not as great as observed by VAN DER HEIJDE⁶ in the case of pyridine.

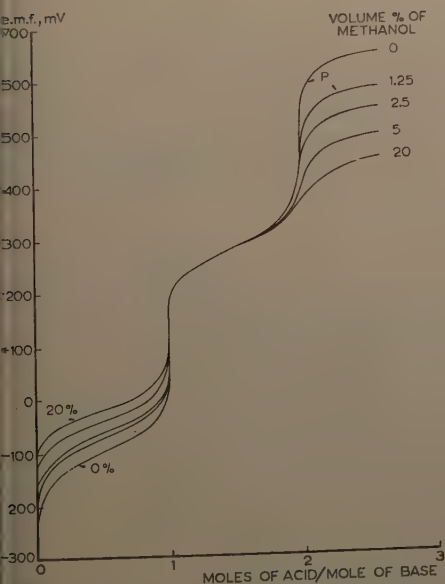


Fig. 7. Potentiometric titration of N, N, N', N'-tetramethylethylenediamine in methanol-nitrobenzene mixtures with perchloric acid (*p* = precipitate formation).

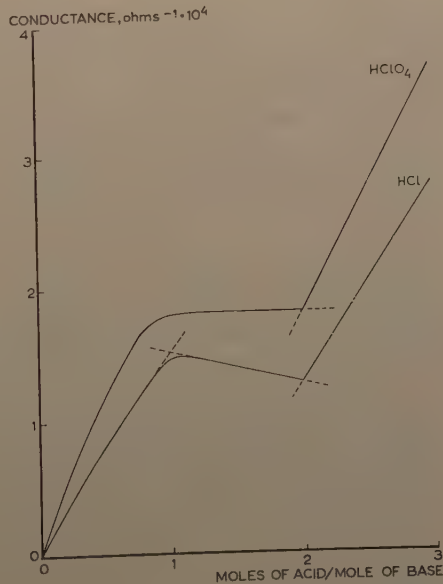


Fig. 8. Conductometric titration of ethylenediamine in methanol-propanol-2 (1 : 1 v/v) with perchloric and hydrochloric acid.

- b. the lower (basic) limit is less sensitive to the solvent composition, but it shows a pronounced decrease at very low methanol content (below 5%). The fact that the value of the second h.n.p. is nearly constant has probably no fundamental significance.
- c. the difference between the first and the second h.n.p. increases with decreasing solvating power.

Dimension of acid anion

Most titrations were carried out with perchloric acid, but hydrochloric acid was used in a few cases in order to study the influence of the acid anion more closely.

From a theoretical standpoint widely different results might be expected when HClO_4 is replaced by HCl (the radii of the anions being 2.6 and 1.8 Å, respectively⁷), but in practice the difference between the curves is not pronounced.

In the potentiometric titrations the curves are, apart from a slight shift, practically identical, and even the difference in the h.n.p. values of the two equivalence points is almost equal: approx. 190 mV when HCl , and about 200 mV when HClO_4 is used.

In the conductometric curves there is a larger difference (Fig. 8) and when hydrochloric acid is the titrant it is possible to determine the first equivalence point with fair accuracy, which cannot be done when perchloric acid is used.

As mentioned above methanolic solvent systems are not ideal for these titrations (especially not for the potentiometric ones) but, when hydrochloric acid is used, methanol must be employed, as most chlorides are insoluble in solvents with lower solvating power.

Influence of distance between the basic groups

The titration of diamines having different numbers of methylene groups between the two nitrogen atoms gave, in general, curves which could be predicted from the results obtained with the dibasic acids⁵, viz. N-shaped conductometric titration curves for compounds such as ethylene- or trimethylenediamines and their derivatives, but no N-shaped curves for the higher members of the series of the aliphatic diamines, e.g. hexamethylenediamine (Fig. 9).

The shapes of the potentiometric curves are analogous to those of the conductometric ones, the ethylene- and trimethylenediamines giving two inflections, hexamethylenediamine only one—viz. the second—(Fig. 10). From these titration curves we may conclude that the difference between the two basicity constants is greater for ethylenediamine than for the substituted trimethylenediamine.

A remarkable exception was found for the methylenediamine derivative (Figs. 9 and 10). In the conductometric titrations an N-shaped curve was never obtained, which is probably due to the structure of this compound. In the potentiometric determinations, however, two inflections are observed, both in solvating and non-solvating media (methanol and nitrobenzene). It may be supposed that the basic groups influence each other inductively through the methylene group.

The influence of steric effects is demonstrated by the behaviour of two cyclohexanediamines, viz. a (technical) 1,3- and a (technical) 1,4 isomer. Both compounds give an N-shaped titration curve in suitable solvents. For the former compound it is less pronounced than for 1,3-diaminopropane and its derivatives (*cf.* Figs. 9 and 11).

the case of 1,4-diaminocyclohexane the N-shape is still less pronounced. The explanation of these phenomena will be given elsewhere.

In the potentiometric titrations the steric influence is of the same order: nitrobenzene is the only solvent in which two distinct inflections are observed, while, as a result of the factors outlined above, the distance between the two h.n.p. values is smaller for both diaminocyclohexanes than for the 1,3-diaminopropane compound.

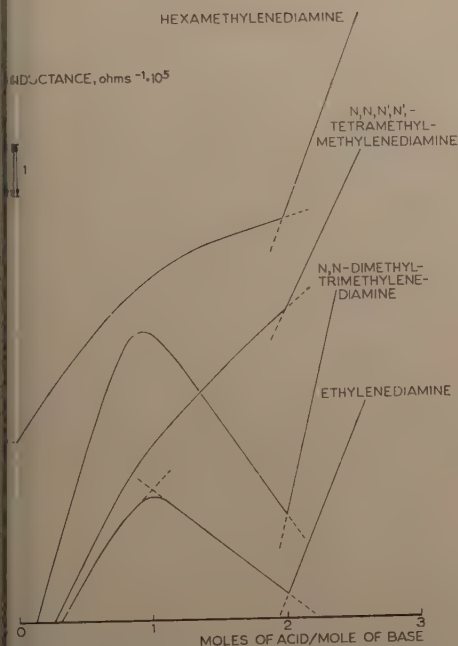


Fig. 9. Conductometric titration of diamines of different chain length in propanol-2 with perchloric acid (curves have been shifted vertically for clarity).

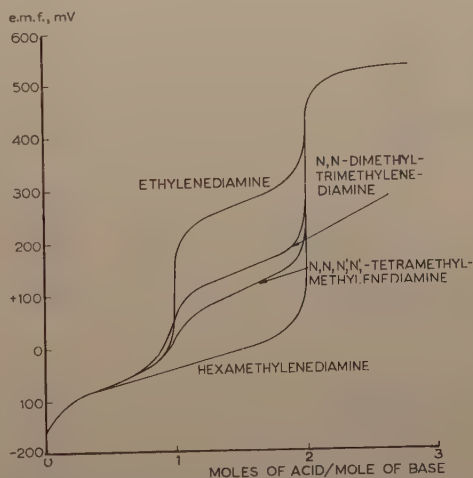


Fig. 10. Potentiometric titration of diamines of different chain length in nitrobenzene containing 2.5% v/v methanol with perchloric acid.

Influence of temperature

In the potentiometric titrations the effect of temperature is hardly noticeable; the distance between the two half-neutralization potentials is in general constant within the experimental error (10–20 mV).

The results of the conductometric titrations are completely analogous to those obtained for the dibasic acids⁵, in that at elevated temperature the N-shape of the curve is more pronounced than at room temperature (Fig. 12). No exceptions to this rule have been observed. In these titrations a complication arises, however, when at higher temperatures mixtures of an alcohol and a hydrocarbon are used as solvents. Then, contrary to what is usually observed, the conductance of the solutions may decrease when the temperature is raised (Fig. 13). At the same time it is seen that the apparent sharpness of the N-curve diminishes. The explanation of these phenomena, which depend on the composition of the solvent mixture, will be given

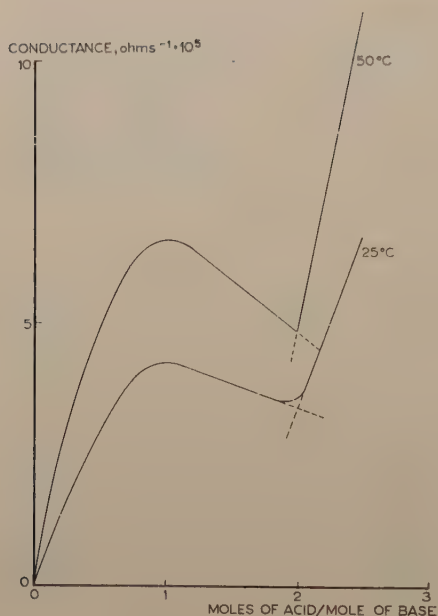


Fig. 11. Conductometric titration of 1,3-diaminocyclohexane in propanol-2 with perchloric acid at different temperatures.

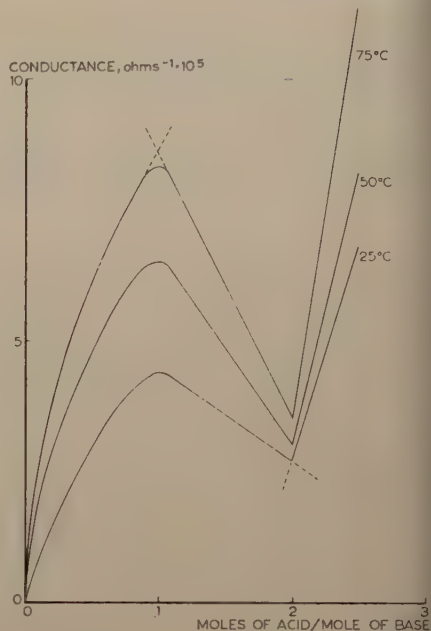


Fig. 12. Conductometric titration of ethylenediamine in propanol-2 with perchloric acid at different temperatures.

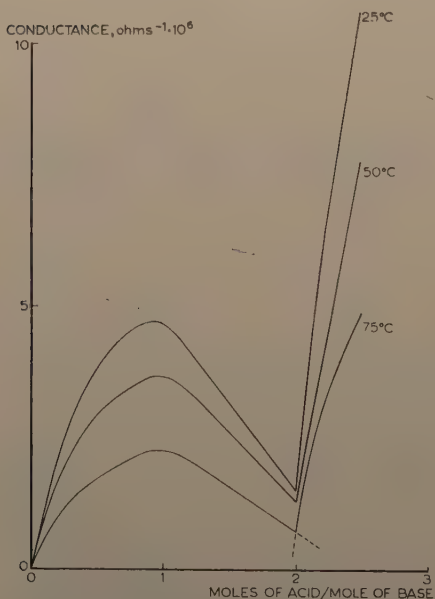


Fig. 13. Conductometric titration of ethylenediamine in propanol-2-benzene (1 : 1 v/v) with perchloric acid at different temperatures.

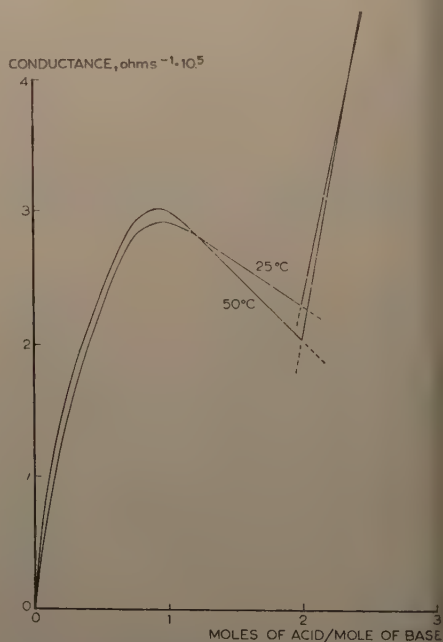


Fig. 14. Conductometric titration of ethylenediamine in ethanol-benzene (5 : 7 v/v) with perchloric acid at different temperatures.

ewhere. If the conditions are chosen such that the conductance at 25° is approximately equal to that at 50°, the N-shaped titration curve becomes visibly sharper again (Fig. 14) just as above.

TITRATION OF MIXTURES

From the foregoing it is clear that the potentiometric method is the more favourable one for differentiating titrations. As an example the titration of a mixture of three bases in nitrobenzene with perchloric acid is shown in Fig. 15. The addition of non-polar solvents to the nitrobenzene results in curves of the same general type (*cf.* Fig. 4).

Other solvents the differentiation is less clear, as can be seen from Figs. 3, 6 and 7. Hence nitrobenzene, either pure or diluted with non-polar solvents, is by far the most suitable for the titration of mixtures of organic bases*.

The application of conductometric titrations to the analysis of mixtures of bases is restricted to a few cases, in particular mixtures of a monovalent and a bivalent amine (ethylenediamine). This titration is illustrated in Fig. 16 from which it is seen that a rise in temperature results in a better determination of the first equivalence point (diethanolamine + half of the ethylenediamine) and hence in a more accurate analysis.

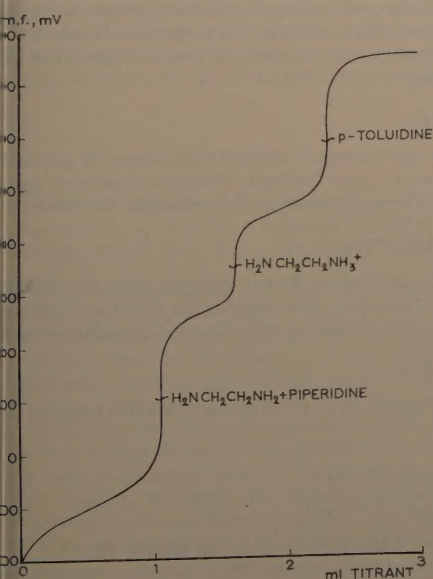


Fig. 15. Potentiometric titration of a mixture of piperidine, ethylenediamine and *p*-toluidine in nitrobenzene with perchloric acid.

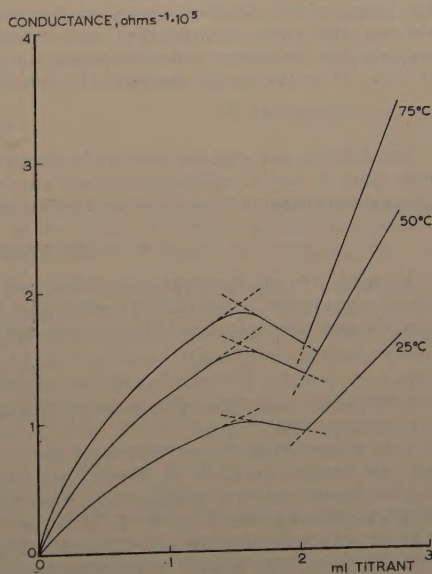


Fig. 16. Conductometric titration of a mixture of diethanolamine and ethylenediamine in propanol-2 with perchloric acid at different temperatures.

CONCLUSIONS

From our experiments we can draw the following conclusions:

I. The factors affecting the shape of the conductometric titration curve are the

* For the potentiometric titration of acids, especially dibasic ones, nitrobenzene is less suitable than pyridine, owing to the low solubility of these compounds in non-solvating media.

same for bivalent bases as for dibasic acids, *viz.* solvent, titrant, distance between the functional groups in the solute molecule and temperature.

2. To determine basic compounds in non-aqueous media the potentiometric procedure is better than the conductometric one, especially when one is dealing with mixtures.

3. A chemically inert medium having a low solvating power but sufficient conductivity is the most suitable for these titrations. An example of this type of solvent for potentiometric titration is nitrobenzene.

ACKNOWLEDGEMENT

The authors are much indebted to Miss A. SNIP, who skilfully carried out many of the titrations. They wish to express their gratitude to Dr. Ir. P. N. DEGENS, Jr. for his stimulating interest in this investigation.

SUMMARY

This paper describes an experimental study of the conductometric and potentiometric titrations of nitrogen bases in non-aqueous media. It is shown that for bivalent bases the factors governing the shape of the titration curve are the same as those previously found for dibasic acids, *viz.* solvent, acid anion, temperature, and distance between basic groups. With the aid of this knowledge a new indifferent solvent system for potentiometric titrations has been developed, which is very attractive for the analysis of mixtures of bases.

RÉSUMÉ

Les auteurs ont effectué une étude expérimentale des titrages conductométriques et potentiométriques de bases organiques en solvants non-aqueux. Les résultats obtenus montrent que la méthode potentiométrique convient particulièrement bien à l'analyse de mélanges de bases.

ZUSAMMENFASSUNG

Es wird über ein konduktometrisches und potentiometrisches Titrationsverfahren zur Bestimmung organischer Basen in nicht-wässrigem Medium berichtet. Die erhaltenen Ergebnisse zeigen, dass die potentiometrische Methode sich besonders gut zur Analyse von Basen-Gemischen eignet.

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REVUES DE LIVRE

Gaz Chromatographie 1958, Edité par D. H. DESTY, Butterworths Scientific Publications, London, 70 s., by post 2s.3 d. extra; Academic Press Inc., New York, 383 pages, \$ 13.00.

En mai 1958 s'est tenu un Symposium au „Royal Tropical Institut" d'Amsterdam, sous les auspices du groupe de recherches de l'Institut du pétrole et de l'Association des chimistes néerlandais, ayant pour objet la chromatographie gazeuse. Cette méthode relativement récente a pris un développement considérable car elle offre des possibilités étonnantes de séparation. Elle permet, du même coup, le dosage des constituants étudiés avec une bonne précision. La rapidité n'est pas l'une des moindres qualités de processus. Les derniers progrès de la „gaz chromatography" ont été présentés à ce Symposium et les exposés réunis en un volume fort bien venu et écrit, dans un temps record, par D. H. DESTY. Cet ouvrage est richement illustré de graphiques, de dessins et de photographies, chaque sujet est suivi des références bibliographiques qui s'y rapportent et d'un résumé de la discussion à laquelle il a donné lieu.

L'ouvrage comprend trois sections d'égale importance. La première traite des diverses bases théoriques de la chromatographie gazeuse, dont nous citerons, par exemple, l'efficacité des colonnes, les isothermes d'adsorption et le comportement chromatographique des vapeurs, la diffusion, la détermination des coefficients d'activité à l'infini, la chromatographie des gaz fortement radioactifs, ...; la seconde partie a pour objet la technique et l'appareillage; on y trouve une foule de données pratiques fort précieuses pour les spécialistes: les divers processus de détections, la construction des colonnes à grande échelle pour la séparation des hydrocarbures, l'utilisation des colonnes multiples ... Enfin, la troisième section est réservée aux exposés traitant plus spécialement des applications tels que l'automatisation, la séparation et le dosage des halogènes volatils, l'analyse des huiles essentielles, la séparation des dérivés d'acides aminés, l'utilisation du sucre comme phase stationnaire pour la séparation des phénols, l'application des hautes températures dans l'industrie du pétrole, etc. La présentation est parfaite, les textes sont clairs et précis. Ce livre apportera à celui qui est au courant des principes de la chromatographie gazeuse des renseignements de première main sur les derniers perfectionnements et possibilités de cette élégante méthode.

D. MONNIER (Genève)

Recommended Methods for the Analysis of Trade Effluents, présentées par un Comité comprenant l'Association of British Chemical Manufacturers" et la „Society for analytical Chemistry", publiées par la „Society for analytical Chemistry" par W. Heffer & Sons Ltd, 1958, 124 pp.

Les eaux usées rejetées par l'industrie contribuent toujours davantage à polluer lacs et rivières. C'est pourquoi, dans la plupart des pays, les gouvernements ont promulgué des lois sévères pour tenter de ralentir ce phénomène. Ceci implique un contrôle minutieux des eaux et provoque aussi des contestations et des procès. Il s'agit donc d'établir des méthodes d'analyses présentant une absolue sécurité et ce problème n'est pas aisé car les eaux résiduaires peuvent renfermer les substances les plus variées. On doit donc être reconnaissant aux analystes anglais d'avoir entrepris cette tâche. Cet ouvrage comprend, outre la préface, 5 chapitres qui sont: Chapitre I, l'échantillonnage, Chapitre II, l'étude préliminaire de l'échantillon avec comme paragraphes principaux: couleur, la température, le pH, la transparence, les suspensions, le résidu d'évaporation, les solides dissous, la dureté, le calcium et le magnésium. Le chapitre III traite du très important problème de la demande en oxygène, une sorte de mesure de la pollution organique; il comprend le titre en permanganate, le titre en dichromate, l'oxygène dissous, la demande biologique en oxygène. Le chapitre suivant comprend les méthodes de dosage des contaminants métalliques, Sb, As, Ba, Cd, Cr, Cu, Fe, Mn, Hg, Ni, K, Se, Na, Zn ... et le dernier chapitre des contaminants non métalliques tels que: carbone organique, chlorure, chlore résiduel, cyanure, thiocyanate, tensioactifs synthétiques anioniques, cationiques et non ioniques, fluorure, formaldéhyde, azote combiné, phénols, phosphore et soufre combiné.

Chaque méthode y est clairement décrite de telle sorte que même des chimistes non spécialisés puissent l'appliquer sans difficulté. Outre le principe de chaque méthode, les auteurs donnent les limites de concentrations pour lesquelles celle-ci est applicable: les réactifs utilisés, le mode opératoire et les interférences principales. On se demande pourquoi les auteurs n'ont pas donné l'erreur standard, la limite de confiance ou même simplement l'ordre de grandeur pour chaque méthode décrite.

Il n'en reste pas moins que ce livre doit être vivement recommandé car chaque méthode a été soignée et présentée avec beaucoup de soin.

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BUCHBESPRECHUNG

Chromatographische Methoden in der analytischen und präparativen anorganischen Chemie unter besonderer Berücksichtigung der Ionenaustauscher, von EWALD BLASIUS, 139 Abb., 40 Tab., xx + 369 Seiten, geheftet DM 96.—, ganzleinen DM 99.—; *Die Chemische Analyse*, herausgeg. von Prof. Dr. GERHART JANDER, 46. Band, Ferdinand Enke Verlag, Stuttgart, 1958.

Der Enke Verlag hat kürzlich seiner Serie „*Die Chemische Analyse*“ einen neuen Band hinzugefügt, der zweifellos den Beifall der Chemiker finden wird. Es ist in der Tat sehr erfreulich, dass die deutsche Chemieliteratur nach dem Kriege solche bedeutende Werke wie das vorliegende aufweisen kann und somit auf diesem Gebiet wie bisher an erster Stelle bleibt.

Dr. E. BLASIUS kommt die Ehre zu, durch langwierige Arbeit sämtliche Anwendungen der Chromatographie auf dem Gebiet der analytischen und anorganischen Chemie in einem Band zusammengefasst zu haben. Das Wort Chromatographie muss hier in seinem weitesten Sinn aufgefasst werden. Wie sich dem Titel des Buches nach schliessen lässt, misst der Verfasser den Ionenaustauschern grösste Bedeutung bei.

Der Text ist klar und auch weniger erfahrenen Chemikern verständlich ohne dadurch für Fachleute an Interesse zu verlieren. Der Literaturnachweis ist reichhaltig, da Dr. E. BLASIUS die Veröffentlichungen bis Ende 1956 systematisch verfolgte. Ausserdem enthält das Werk einerseits eine Auswahl kürzlich erschienener Abhandlungen und andererseits zahlreiche von ihm selbst bisher nicht veröffentlichte Arbeiten.

Anschliessend gebe ich eine kurze Übersicht der Kapitel: 1. Übersicht; 2. Die physikalisch-chemische Behandlung der Probleme; 3. Das Adsorbens; 4. Das Arbeitsmedium, Wechselwirkung Ion-Lösungsmittel-Adsorbens; 5. Apparaturen für die Säulenchromatographie; 6. Verwendung von Ionenaustauschern; 7. Verwendung weiterer Adsorbentien in der Säulenchromatographie; 8. Papierstreifen oder Bögen; 9. Ionophorese auf Trägermedien, Elektrochromatographie; 10. Austauschmembranen.

Es ist zu hoffen, dass dieses ausgezeichnete Werk möglichst bald übersetzt werde, damit es Fachleuten anderer Länder zugänglich wird. Ich empfehle es wärmstens den Analytikern und diejenigen, die sich mit der anorganischen Chemie beschäftigen, in der Überzeugung, dass es für ihre Arbeit äusserst wertvolle Hinweise enthält.

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ANNOUNCEMENT

The Eleventh Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Penn-Sheraton Hotel in Pittsburgh, Pennsylvania, U.S.A., from February 29 through March 4, 1960.

Original papers are invited on all phases of analytical chemistry, spectroscopy, and nucleonics applied to analysis. The final date for receipt of abstracts is October 15, 1959. Two abstracts should be submitted in triplicate. The first abstract should be limited to 150 words to be printed in the program. The second abstract should be of approximately 500 words to help the Program Committee evaluate and classify the paper. A letter sent with the abstracts should list the names of authors, laboratory in which the work was done, and the current addresses of the authors. All correspondence should be addressed to:

JAMES E. PATERSON, Program Chairman
The Eleventh Annual Pittsburgh Conference
Jones & Laughlin Steel Corporation
Graham Research Laboratory
Pittsburgh 30, Pennsylvania

In addition to the program of technical papers, there will be an exhibition of the newest instrumentation for analysis. More than seventy-five companies will display instruments, chemicals, and equipment.